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Speciation of Hazardous Inorganic Compounds by Fourier Transform Infrared (FTIR) Spectroscopy

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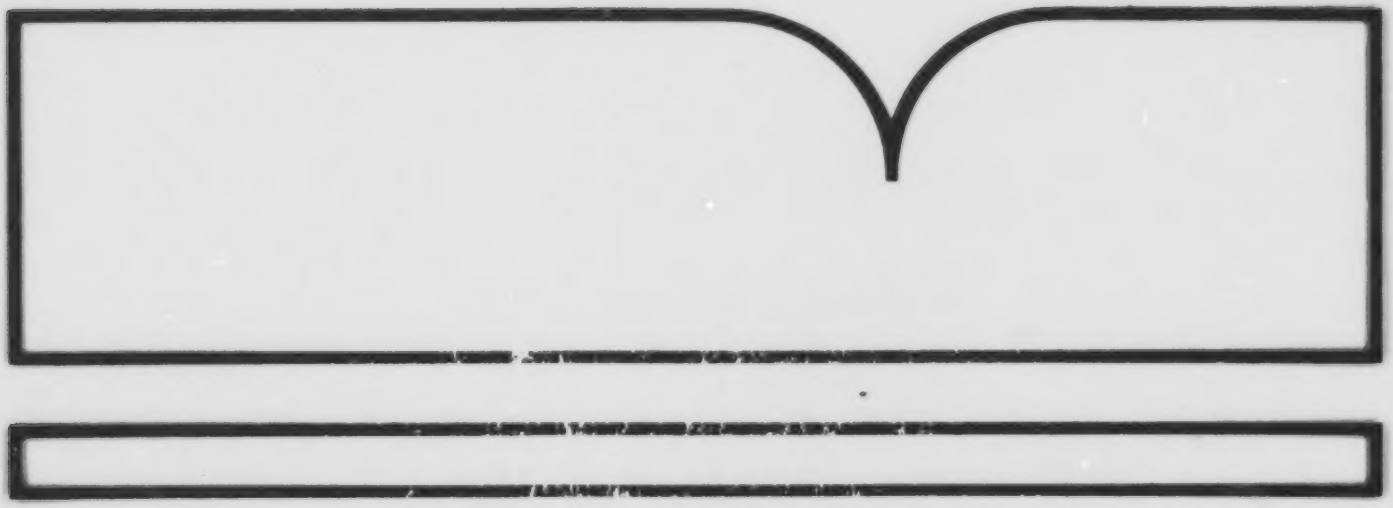

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SPECIATION OF HAZARDOUS INORGANIC COMPOUNDS BY FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

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16. ABSTRACT The report describes an extension of the application of infrared methodology to characterize hazardous inorganic compounds in solid inorganic emissions, based on recent advances in instrumentation for Fourier transform infrared (FTIR) spectroscopy. The improved instrumentation, consisting of multiple-scan computer enhancement methods, has increased the signal-to-noise ratio so that low concentrations on infrared active bands are now measurable. The ability to use spectral subtraction methods, together with improved infrared detectors, also permits trace level infrared analysis; a few years ago, this was not possible. Increasing the infrared spectral scanning range to the far infrared (i.e., down to 100 reciprocal cm) permits characterization of metal-oxygen bending modes. The result of this enhanced technology allows the speciation of hazardous inorganic compounds.

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Inorganic Compounds	Stationary Sources	07B
Toxicity	Hazardous Inorganics	06T
Infrared Spectroscopy	Speciation	14B
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ABSTRACT

Recent advances in instrumentation for Fourier transform infrared (FTIR) spectroscopy have provided the opportunity to extend the application of infrared methodology to characterize hazardous inorganic compounds in solid inorganic emissions. The improved instrumentation, consisting of multiple-scan computer enhancement methods, has increased the signal-to-noise ratio so that low concentrations of infrared active bands are now measureable. Also, the ability to use spectral subtraction methods, together with improved infrared detectors in the past ten years permits trace level infrared analyses, where a few years ago this was not possible. By increasing the infrared scanning range to the far infrared, i.e., down to 100 cm^{-1}, permits characterization of metal-oxygen bending modes. The result of this enhanced technology permits the speciation of the hazardous inorganic compounds.

In this task, gaps in the available, relevant inorganic compound spectral data base were identified and a series of reference infrared spectra were obtained. These served as a basis for characterizing hazardous inorganic compounds obtained from emissions collected from metal smelting operations, a steel mill, and a fluidized bed desulfurization control process. Special studies were conducted to determine the effect of water on far infrared spectra (500 to 100 cm^{-1}). Typical environmental samples provided by the Industrial Environmental Research Laboratory were examined using the techniques developed in this task. In addition, studies were undertaken to determine the effect of matrix interferences on the dilutant spectra and potential matrix isolation techniques consisting of spectral subtraction methods and chemical extraction approaches were examined. Further, the use of attenuated total reflectance (ATR) was studied as a means to measure potentially hazardous inorganic compounds which accumulate on the surface of fly ash and as a technique to facilitate sample preparation.

This study demonstrated that FTIR was a useful analytical chemistry technique for inorganic compound speciation. The mid infrared region provided information regarding the anionic groups and the far infrared region provided information regarding the metal and its oxidation state, principally from the metal oxygen bending modes. A useful chart showing the absorption frequency as a function of nineteen different inorganic compounds over the mid infrared and far infrared range was prepared and found useful in making structural assignments.

Using FTIR instrumentation, it appears that infrared spectroscopy will be a valuable tool for inorganic compound characterization just as conventional infrared spectroscopy has for characterization of organic compounds.

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SECTION 1

INTRODUCTION

Recent studies conducted at S-CUBED and elsewhere (1,2) imply that the extent of toxicity of fly ash, other coal-fired utility waste, and high-temperature metal processing emissions depends directly on the trace elemental composition and the specific compounds on the surface of the waste and within the waste. The compound configuration is important for two reasons:

(1) The inherent toxicity of the compound, and

(2) The ability of the compound to be mobilized (e.g., by a leaching process) to become available and introduced into the environment.

An example of the variability in toxicity for five different mercury compounds is shown in Table 1. While the relative mercury content (compared to mercuric oxide) ranges from only 0.73 to 1.0, the calculated human LD_{50} varies by a factor of over 16. In addition to the toxicity variation among the compounds, there are considerable differences in solubility and hence the potential for becoming mobilized, which is also compound-assemblage (molecular configuration) related. In addition to the information regarding mercury compounds shown in Table 1, the differences in the toxicity of arsenic oxide compound form, e.g., As_2O_3 and As_2O_5, have been well chronicled (3,4).

In a combustion process, it has been determined that trace metals concentrate on the surface of particles (5,6). Consequently, the concentration of the trace metal available for introduction into aqueous waterways is much higher during the initial contact and not directly related to the average composition of the trace metal within the amorphous fly ash matrix. Consequently, in order to obtain and understand the environmental impact of solid fossil fuel combustion products, waste incineration or metal smelting processes, it is essential to establish methodology capable of characterizing the specific compound form or molecular assemblage of the trace materials present.

Currently, there are few analytical chemistry techniques capable of characterizing toxic compounds present on the surface of hazardous inorganic waste. Auger, ESCA and Ion Microprobe provide supporting information regarding surface composition, but not always definitive information and at higher cost. Particularly, hazardous inorganic wastes are often amorphous in structure; thereby limiting the use of X-ray techniques. Time-resolved solvent leaching (7) is one approach that will permit speciation of surface materials; however, it is limited to the selective removal of a single compound at a time and requires extensive periods for characterizing of a series of pollutant compounds. On the other hand, the use of infrared spectroscopy permits the opportunity to identify and provide information about noncrystalline inorganic compounds. Furthermore, the use of Fourier transform infrared (FTIR) spectroscopy extends the application of infrared to qualitate

TABLE 1. RELATIONSHIP OF MERCURY COMPOUND FORM TO TOXICITY AND SOLUBILITY

Compound	Relative Hg Concentration*	Calculated Human LD mg/kg	Solubility in H_2O g/100 mL
HgO	1.00	3	0.0052
$HgCl_2$	0.80	6	6.9
$HgSO_4$	0.73	9	0.06
HgCl	0.92	34	0.0002
$HgNO_3$	0.82	48	very soluble

*Relative to HgO

the presence of spectrally active compounds at low concentrations through (1) the signal-to-noise enhancement characteristic of FTIR and (2) the facile ability to use spectral subtraction methods.

The recent advent of improved instrumentation for FTIR spectroscopy has provided the opportunity to measure infrared vibration and bending modes in a wider frequency range down to 100 cm^{-1}. This infrared range is specifically active to inorganic compounds (8). Furthermore, the advances in instrumentation, which have utilized cryogenically cooled, photoconducting detectors having enhanced signal-to-noise characteristics, permit infrared measurement sensitivities at levels never before attained, e.g., in the nanogram quantities in the mid infrared range. The consequence of these improvements permits trace level infrared analyses, where a few years ago they were not possible.

The objective of this task was to evaluate the applicability of Fourier transform infrared spectroscopy for characterization of toxic compounds at low to trace concentration levels in hazardous inorganic wastes. The infrared spectral range for this study was 4000 to 100 cm^{-1}. The potassium bromide pellet sample preparation technique was employed for the spectral range of 4000 to 400 cm^{-1}; polyethylene sample preparation techniques were employed for the spectral range of 500 to 100 cm^{-1}.

The task effort was divided into six separate subtask elements aimed to develop a technical understanding of various aspects of the speciation of inorganic compounds in the infrared and sampling and measurement parameters which may affect the interpretation of data. Specifically, the task elements were:

Subtask 1 - Identify Gaps in Available, Relevant Inorganic Compound Spectra -- A list of potentially hazardous inorganic compounds whose spectra had not been obtained with state-of-the-art instrumentation or suitable matrices for optimum detection sensitivity was compiled. Using this list as a basis, a number of compounds were selected for study.

Subtask 2 - Generate Reference Infrared Spectra -- Reference infrared spectra range of 4000 to 100 cm^{-1} will be obtained on compounds selected in Subtask 1.

Subtask 3 - Determine the Effect of Water on Far Infrared Spectra -- The interference of water in the far infrared spectra range (500 to 100 cm^{-1}) will be qualitated and techniques for obtaining valid spectra in this range will be identified.

Subtask 4 - Characterize Environmental Samples for Trace Level Chemical Compounds -- Typical environmental samples will be acquired from EPA and characterized by FTIR. The effect of matrix interferences will be determined.

Subtask 5 - Investigate Potential Methods to Eliminate Sample Matrix Effects -- Spectral subtraction methods and chemical extraction approaches will be investigated.

Subtask 6 - Investigation of the Use of Attenuated Total Reflectance -- The measurement of potentially hazardous inorganic compounds which accumulate on the surface of fly ash will be investigated.

The conclusions of this study and recommendations generated as a result of this project are presented in Sections 2 and 3, respectively. Details on the experimental studies conducted in performing the six subtask activities are presented in Section 4, and Appendix A provides reference FTIR spectra generated during this task for potential hazardous inorganic compounds.

SECTION 2

CONCLUSIONS

Fourier Transform Infrared Spectroscopy (FTIR) was shown to be a useful analytical chemistry technique for inorganic compound speciation. The mid infrared region provided information regarding the anionic groups and the far infrared region provided information about the metal and its oxidation state, principally from the metal oxygen bending modes. This project clearly demonstrated the feasibility of FTIR for qualitative characterization of inorganic compounds. It now appears that FTIR infrared spectroscopy will be a valuable tool for inorganic compound characterization, just as conventional infrared spectroscopy has served for many years to characterize organic compounds. The reason for this is that inorganic compounds have characteristic fingerprint infrared spectra which are similar to the fingerprint region for organic compounds.

The findings of this task effort are as follows:

(1) There was very little information available in the literature regarding FTIR and its application to inorganic compound speciation. The spectra of a number of environmentally significant inorganic compounds were analyzed from low resolution NaCl prism instruments.

(2) Of the nineteen different compounds evaluated, each had its own characteristic infrared spectra. Some of the compounds had similar mid or far infrared spectra, but no two compounds had the same overall spectrum (in the range 400 to 100 cm^{-1}).

(3) A useful "Colthup"-type chart was prepared which shows the set of absorption frequencies for each inorganic compound studied. This chart, although limited with only nineteen inorganic compounds, was found to be useful in making structural assignments based on a set of absorbance frequencies.

(4) Incorporation of water in the form of water of hydration did modify the far infrared spectrum of inorganic compounds because the water caused a change of molecular structure.

(5) Spectral substraction methods for eliminating background sample matrix interferences were found to be limited unless clear-cut identification of the sample matrix had been made.

(6) Sample matrix interfering absorptions made quantitation of the pollutant in the sample difficult unless its concentration was at levels of one percent or higher.

(7) Improved methods for rapid characterization of matrix interferences are required to make FTIR a more consistent, viable analytical tool.

(8) The feasibility of FTIR to identify toxic inorganic compounds in environmental samples from smelter flue gas, a fluidized bed combuster effluent, and a steel mill effluent particulate matter was demonstrated.

(9) The use of attenuated total reflectance (ATR) for sample preparation permitted FTIR methodology to provide information regarding the differences between surface composition of particles and their bulk composition. The ATR was only useful in the mid infrared region; therefore, it only provided useful information regarding anionic groups in the inorganic molecular assemblage.

SECTION 3

RECOMMENDATIONS

Additional information is required to extend the utility of infrared characterization of environmental samples. Needed information is in the areas of (1) increasing the library of available reference spectra, (2) verify its applicability for characterization of environmental samples, and (3) development of improved methodology for characterization of environmental sample matrix materials and concentration of toxic pollutants in environmental samples. The need for more reference spectra is important because expanded correlation tables must be developed to cover the probable inorganic compounds that might be emitted from commercial manufacturing, power conversion and hazardous waste treatment methods (e.g., incineration).

The characterization of environmental assessment samples by FTIR is accomplished through a series of three separate activities:

(1) Sample preparation,

(2) Acquisition of spectra, followed by

(3) Its qualitative analysis interpretation.

Sample preparation techniques that need to be developed further are aimed at differential separation/isolation of the pollutant to be measured from its matrix, either through concentration of the matrix, or the pollutant. Once the background matrix has been identified, usefulness of FTIR increases significantly as an analytical tool. If a background matrix cannot be identified, only compounds present in the environmental sample at the level of one percent and above can be identified readily.

Qualitative analysis takes two forms: (1) direct identification of compounds by interpretation of the infrared spectrum through comparison with reference information, or (2) use of spectral subtraction techniques to isolate the pollutant from its matrix. Clearly, interpretation of the infrared spectra will improve as additional reference spectra of candidate pollutants and matrices are acquired. The spectral subtraction methodology has limited use, but can only be employed when the background matrix is identified.

To increase the utility of FTIR for inorganic compound characterization in environmental samples, it is essential to incorporate a concentration step which may be enhanced by spectral subtraction methodology. Qualitative analysis depends on the type of material present in the sample. Some compounds are weak infrared absorbers and can be masked out by the matrix, while other compounds have strong absorptions that can be readily identified. For characterization analysis to be successful, the chemical nature of the matrix has to be identified. Special sample preparation techniques must be employed both to (1) facilitate the identification of the matrix material and (2) concentrate the pollutant to be identified. All sample preparation techniques must emphasize concentration of the pollutant to increase the sensitivity of detection.

The findings of this task clearly show the feasibility of FTIR for characterizing inorganic structural compound assemblages. The partial success at identifying pollutants in environmental samples is the basis of our recommendation for (1) further study using additional environmental samples, (2) new approaches for selective differentiation of the pollutant and its matrix, and (3) examination of a wider range of potential compounds.

SECTION 4

EXPERIMENTAL STUDIES

This section provides discussions on the experimental studies conducted in performing the six task activities. Information provided in this section is supported by reference spectra generated during the project and presented in Appendix A.

4.1 SUBTASK 1 - IDENTIFY DATA GAPS IN AVAILABLE, RELEVANT INORGANIC COMPOUND SPECTRA

The current technical literature was reviewed to determine how infrared spectroscopy had been applied to the characterization of inorganic matter. The basic assumption for this task centered upon lack of direct application of infrared spectroscopy in both the mid and especially the far infrared region to characterize inorganic matter. Because of the lack of existing data for infrared spectroscopy of inorganic matter, the infrared spectra of potentially hazardous compounds or environmentally significant compounds were considered to be nonexistent, particularly as determined by a modern FTIR spectrometer.

A review of the current literature for infrared spectra of potentially hazardous inorganic compounds has been conducted. The guidelines for the literature search were the following:

(1) Spectral range of 4000 to 100 cm^{-1}.

(2) Spectra had to be acquired by an FTIR instrument.

(3) Sample matrices preferred were KBr (4000-400 cm^{-1}) and polyethylene (500-100 cm^{-1}).

(4) Only articles cited after 1965 were reviewed.

The literature sources reviewed were:

- Analytical Chemistry (1965-1980)
- Applied Spectroscopy (1965-1980)
- Chemical Abstracts (1965-1980)
- Environmental Science and Technology (1966-1980)
- Spectrochemical Acta PRTA: Molecular Spectroscopy (1967-1980)
- Spectroscopic Properties of Inorganic and Organometallic Compounds (1968-1978)
- Spectroscopy Letters (1968-1980)

- Journal of Inorganic and Nuclear Chemistry (1965-1980)
- Coblentz Society Infrared Reference Spectra, Sadtler Reference Spectra - Inorganic IR Grating (1967)
- "Infrared Spectra of Inorganic and Coordination Compounds" by K. Nakamoto (8)
- "Infrared Spectra of Inorganic Compounds (3800-45 cm^{-1})" by Nyquist, R.A. and Kagel, R.O (9)
- "Inorganic Infrared and Raman Spectra" by Ross, S.D. (10)

The literature review indicated that large data gaps existed for infrared spectra of potentially hazardous inorganic compounds. The most valuable reference found was that by Nyquist and Kagel (9). This volume provided both mid infrared and far infrared spectra of a number of inorganic compounds. Their compound compilation was incomplete for the purposes of this task, and in all cases spectra reported were obtained using spectrometers equipped with grating monochrometers. Two pertinent articles by Grendreau, et al. (11,12), were located. Both articles cited dealt with $CaSO_4$ in a KBr matrix. Besides the limited amount of inorganic spectra available, far infrared spectra of inorganic compounds were almost nonexistent. Based upon the literature review, a list of 96 environmentally significant compounds whose spectra were not available was compiled. Table 2 provides a list of the 14 compounds missing FTIR spectra which are not commercially available. The list of compounds which are commercially available (82) is presented in Table 3.

A series of articles which were outside the guidelines of this subtask, but would be of interest for inorganic speciation, was written by Paul C. Painter, et al. (13 through 17). These articles deal with the application of FTIR to the determination of mineral matter in coal and oil shale. These articles did not directly apply to the objectives of the task, but provided a good background for infrared spectroscopy of inorganic material.

TABLE 2. ENVIRONMENTALLY SIGNIFICANT COMPOUNDS WHICH ARE NOT READILY AVAILABLE AND NO FTIR SPECTRA EXISTS

Nitrates	Chromates	Phosphates	Arsenites
Mercury I	Cadmium	Antimony	Antimony
	Silver	Cadmium	Copper
		Chromium	Lead
		Copper	Zinc
		Lead	
		Mercury	
		Nickel	

TABLE 3. ENVIRONMENTALLY SIGNIFICANT COMPOUNDS WHICH ARE COMMERCIALLY AVAILABLE AND NO FTIR SPECTRA EXISTS

Metal	Chlorides	Chromates	Carbonates	Fluorides	Nitrates	Phosphates	Sulfides	Sulfates
Ammonium	x	x	x		x	x		
Antimony III	x			x			x	x
Antimony V	x			x			x	
Arsenic III	x			x			x	
Beryllium	x		x	x	x			x
Cadmium	x		x	x	x		x	x
Chromium	x			x	x		x	x
Copper	x		x	x			x	x
Lead	x	x	x	x	x		x	x
Mercury I	x			x				x
Mercury II	x			x				x
Nickel	x		x	x	x		x	x
Selenium I	x			x			x	
Selenium IV	x			x				
Silver	x		x	x	x	x	x	x
Thallium	x		x	x	x		x	x
Zinc	x	x	x	x	x	x	x	x

4.2 SUBTASK 2 - GENERATE INFRARED SPECTRA OF VARIOUS INORGANIC COMPOUNDS

This effort consisted of obtaining mid and far infrared spectra of (1) potentially hazardous inorganic compounds or (2) environmentally significant compounds. The compounds were selected from the list of 82 candidate commercially available compounds presented in Table 2. The compounds were selected based upon EPA interest for specific compounds and the availability of acquiring the compounds through a commercial source. The 19 compounds selected for generation of infrared spectra were the following:

ammonium nitrate
ammonium sulfate
arsenic (III) oxide
arsenic (V) oxide
calcium sulfate
lead sulfate
mercury (I) chloride
mercury (II) chloride
mercury (I) sulfate
mercury (II) sulfate
sodium chromate
sodium dichromate
sodium metavanadate
sodium nitrate
sodium nitrite
sodium orthovanadate
sodium selenate
sodium sulfate
sodium sulfite

This list was chosen to show how the infrared spectra of the elements and assemblages of concern are present in different compounds. The compounds listed above formed a very diverse and interesting group. These compounds showed the utility of FTIR for the characterization of inorganic material. In terms of simple anion-type assemblage characterization, the group contained nitrate, nitrite, oxide, sulfate, sulfite, chloride, chromate, dichromate, selenate, metavanadate, and orthovanadate. The discrete characterization of the various anion-type groups was facilitated because sodium was the central metal group cation for most of the anions. Consequently, its influence over the metal-nonmetal-oxygen bending and stretching sequences observed would be held constant in direct comparison of spectra; its influence was expected to be of second-order importance.

In terms of metal-anion characterization using comparable anion assemblages, the list of compounds (e.g., chloride, sulfate) contained the two oxidation states of mercury and arsenic, ammonium, calcium, and lead. In these cases, the anion was sulfate; therefore, its contribution to the spectra was controlled. In general, the mid infrared region was employed to characterize the anions. The mid infrared region was most useful for this characterization because the anion of environmentally significant compounds was usually made up of two or more different atoms.

For most inorganic compounds, ionic bonds exist between the metal and the anion group. Ionic bonds are weak mid infrared absorbers. Ionic bonds usually absorb in the far infrared region and are observed as a lattice-type bond vibration. For anions like sulfate, there are two types of bonds present in the compound; the ionic bond between the metal and the sulfate anion, and covalent bond within the radical between oxygen and sulfur. Covalent bonds usually absorb in the mid infrared region. The sulfur-oxygen bond has an absorbance at 1100 cm^{-1}, where the fine structure of the main absorbance would indicate how the anion is bound to the metal, e.g., uncoordinated, unidentate, bidentate, or bidentate-bridge. For simple anions like chloride, which usually bonds uncoordinated, only the weak lattice bond vibration would absorb in the far infrared region.

For central metal identification, the far infrared region was employed. The same discussion considered for the anionic radicals applies to the metal. Again, where a metal is present, the lattice bond vibration showed up in the far infrared. For the ammonium ion, the mid infrared region was employed because of the presence of the hydrogen-nitrogen bond in the central "metal" radical.

4.2.1 Experimental Details

Procedures used for preparation of samples to be analyzed in the mid infrared and far infrared are presented below, together with FTIR spectrometer operational settings.

4.2.1.1 Sample Preparation

The sample for the mid infrared region (4000-400 cm^{-1}) consisted of diluting a known quantity of compound in a KBr pellet. The pellet was made by first mixing 200 mg of infrared optically pure, dried KBr with 1 mg of compound of interest. The mixture was ground into a fine powder with the use of a Wig-L-Bug.* The average time for grinding was five minutes. The fine powder mixture was transferred to a die and pressed into a pellet. The force applied to the die was approximately 20,000 pounds for two minutes. Whenever the pellet was not being used, it was stored in a drying oven.

The sample matrix for the far infrared region (500-100 cm^{-1}) was a polyethylene pellet. Before a pellet could be made, the polyethylene had to be purified. Purification was accomplished by dissolving polyethylene in hot xylene, cooling the solution to room temperature, and then the polyethylene was precipitated with the addition of ethanol. The filtered product was washed with ethanol and dried. The material was then sized with a 120-mesh sieve. The material obtained was sufficiently optically pure for far infrared pellets.

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*Crescent Dental Manufacturing Company

The pellet was made by mixing 100 mg of far infrared optically pure polyethylene and 2 mg of pure sample. The mixture was ground into flakes with the use of a Wig-L-Bug. The average time for grinding was two minutes. The polyethylene-flake mixture was transferred to a special aluminum die for hot pressing.

The hot pressing technique consisted of placing the polyethylene flakes on a flat, smooth aluminum surface, maintained at approximately 100°C. The material was formed into a sphere and a second flat, smooth aluminum plate was placed on top. Both pieces of aluminum were placed into a hydraulic press where a 200-pound force was applied for two minutes. The average thickness of sample was 0.04 cm + 0.01. To obtain a consistent sample thickness, a spacer was placed between the two aluminum plates. Also, the spacer had a large open space so that the polyethylene flowed or was spread out during pressing, and was not confined between the plates.

4.2.1.2 FTIR Spectrometer

The FTIR spectrometer employed in this work was the Digilab Model FTS-15C Fourier Transform Infrared Spectrometer. This instrument has the following features:

- Automatic ratio recording infrared spectrophotomer with resolution of 0.25 cm^{-1}.
- Spectral range: 4000 - 400 cm^{-1}, mid infrared.
- Spectral range: 500 - 10 cm^{-1}, far infrared.
- A Model 396 Michelson Interferometer with KBr beamsplitter for mid infrared and Mylar beamsplitters for far infrared.
- Dual-Beam Optics Triglycine Sulfate Detector (4000 - 400 cm^{-1}).
- Filtered Triglycine Sulfate Detector (500 - 100 cm^{-1}).
- Analog-to-Digital converter and data system with 32K of MOS memory.
- Five-million word, dual-drive moving head disk.
- A Spectromate graphic and alphanumeric operator terminal.

Sample pellets were inserted into the optical path of the infrared spectrometer and spectra were obtained after studying specific operating conditions of scan rate, resolution, number of scans, and spectrum mode (transmittance or absorbance), and output dimensions and range.

4.2.2 Discussion of Results

The 38 reference spectra for the 19 compounds selected for study are presented in Appendix A. A study of the resulting spectra permitted the generation of a "Colthup"-type chart of mid and far infrared absorbance frequency characteristic bands for the inorganic compounds studied over the range 1500 cm^{-1} to 100 cm^{-1}. This chart is presented in Figure 1 and permits the qualitative characterization among these compounds by examination of their mid and far infrared spectral absorbancies. A detailed discussion of the comparisons made among the various spectra is presented below. The spectra provided in Appendix A have been scrutinized and obvious impurity bands for water, carbon dioxide and other contaminants have been rejected and are not shown in Figure 1.

4.2.2.1 Mercury Compounds

The mercury compounds studied were mercury (I) chloride, mercury (II) chloride, mercury (I) sulfate, and mercury (II) sulfate.

Mid Infrared

The mercury element, either in the positive (I) oxidation state or the positive (II) oxidation state, did not absorb in the mid infrared region. The mid infrared region was dominated by the anion assemblage absorbances. For mercury compounds, the mid infrared region only distinguished between the chlorides and the sulfates and not the oxidation states of mercury. Mercury sulfates absorbed in the mid infrared region because of the sulfur-oxygen bond of the anion radical. Because the mercury-chloride bond was mainly linear (therefore, no change in dipole moment), the mercury chlorides did not possess a characteristic mid infrared spectrum.

Far Infrared

Mercury compounds have a far infrared spectrum which consists of lattice bond vibrations characteristic for each oxidation state. Mercury (I) sulfate had the same characteristic spectrum as mercury (I) chloride, one strong absorbance of 250 cm^{-1}. Mercury (II) chloride has a single strong absorbance at 375 cm^{-1}, where mercury (II) sulfate has three absorbances, 415, 315, and 240 cm^{-1}. The combination of far infrared (to identify oxidation state) and the mid infrared (to identify radical anionic compositions) regions permits identification of the inorganic mercury compound.

4.2.2.2 Arsenic Compounds

The arsenic compounds compared were arsenic (V) oxide and arsenic (III) oxide.

Mid Infrared

The spectrum of arsenic (V) oxide was dominated by the water of hydration; this was indicated by the very broad absorbance bands throughout the spectrum. The mid infrared absorbances of the arsenic oxides were

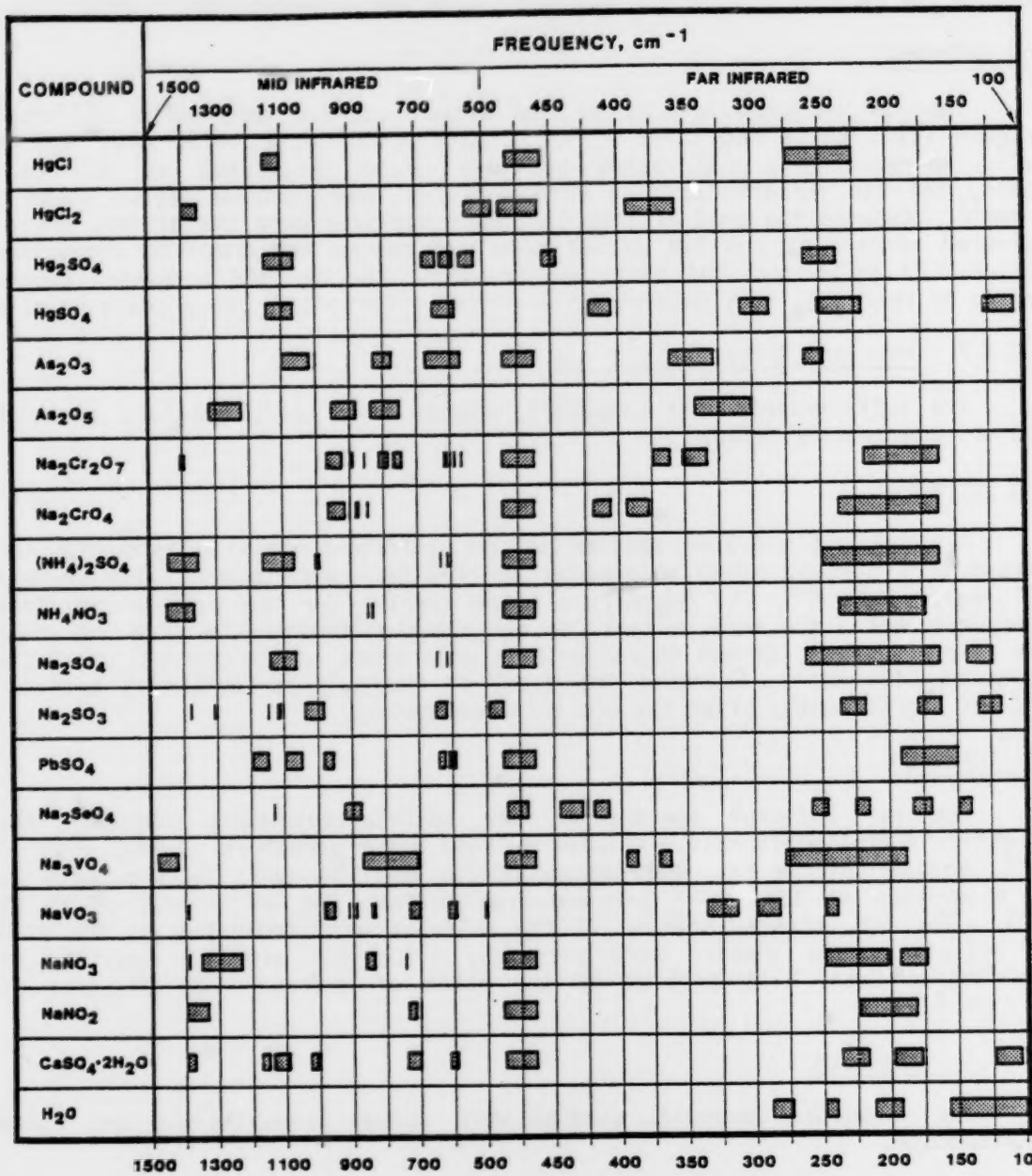


Figure 1. Mid and Far Infrared Absorbance Frequency Characteristics for Inorganic Compounds Studied

different for the positive (III) state and the positive (V) state, but additional information was needed to give a positive identification of the oxidation state. The arsenic compounds had a complex mid infrared spectrum because the molecular structure was not linear and somewhat complicated.

Far Infrared

The far infrared spectra of the arsenic oxides were quite different. Arsenic (III) oxide had three strong, sharp absorbances, 475, 350, and 260 cm^{-1}, where arsenic (V) oxide had one broad absorbance at 325 cm^{-1}. Again, the far infrared spectra were different for each oxidation state of arsenic. Because the only arsenic compounds employed were the oxides, the mid infrared spectra of the two oxides were not needed for complete characterization. If an unknown had contained arsenic, then the mid infrared spectrum had to be recorded, so a determination of the anionic-type group could be made.

4.2.2.3 Compounds Containing Sulfate

The sulfate-containing compounds studied were lead, calcium, ammonium, sodium, and mercury salts.

Mid Infrared

All the mid infrared spectra of the sulfate-containing compounds consisted of a strong, broad absorbance at 1100 cm^{-1} with a weak absorbance at 600 and/or 650 cm^{-1}. In general, all the spectra for the sulfate-containing compounds looked the same, except for the ammonium compound because the ammonium assemblage has its own characteristic absorbance due to the N-H stretching modes at 1400 cm^{-1}. Changing the metal of the sulfate-containing compounds did not significantly alter the mid infrared spectra.

Far Infrared

The far infrared spectra of the sulfate-containing compounds were essentially distinguishable. Calcium sulfate had absorbances of 240, 210, 180 cm^{-1}; sodium sulfate had absorbances at 225 and 140 cm^{-1}; lead sulfate had an absorbance at 155 cm^{-1}; and ammonium sulfate had an absorbance at 210 cm^{-1}. The far infrared spectra of the sulfates were dominated by the water of hydration; the spectra were extremely broad and did not provide good qualitative data. The problem of the water of hydration is discussed in Section 4.3.

4.2.2.4 Vanadates

The vanadates compounds studied were sodium orthovanadate and sodium metavanadate.

Mid Infrared

The infrared spectra for both compounds were different from each other because their structures were dissimilar (orthovanadate - VO_4^{3} and metavanadate - VO_3^{1}), even though vanadium had a positive five oxidation state in both forms. The vanadates presented somewhat of a different example compared to the compounds previously discussed. In this particular case, the metal of interest was part of the anionic radical. The mid infrared spectrum showed the vanadium-oxygen bond within the radical and not the sodium-anionic radical interaction. The vanadate infrared spectra had very broad absorbances, which indicated the presence of water of hydration.

Far Infrared

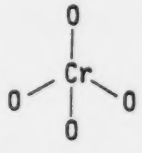
The far infrared spectra of the vanadates were different and this related to the lattice vibration for vanadium anionic group and its position in the crystal structure for each compound. Sodium orthovanadate had absorbances at 475, 400, 375, and 225 cm^{-1}, sodium metavanadate had absorbances at 500 and 280 cm^{-1}.

4.2.2.5 Chromate

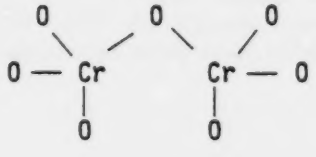
The chromate compounds studied were sodium chromate and sodium dichromate.

Mid Infrared

The comparisons between chromate and dichromate were very interesting because the oxidation state of all the ions was the same, only the structure was different. For the chromate ion, the structure was tetrahedral:



For the dichromate ion, the structure was tetrahedral with a bridging oxygen:



The distinct difference in the infrared spectrum between chromates was due to the Cr-O-Cr bridge. The infrared spectrum of dichromate did have additional absorbances at 750 and 550 cm^{-1} and these were characteristic absorbances for the metal-oxygen-metal bridge structure. Throughout the discussion here,

there have been indications regarding the relationship between the structure of the inorganic compound and its infrared spectrum. The chromate example proved that mid infrared region provided information about structure regardless of the oxidation state of the ion involved. The far infrared provided information in terms of the metals and their oxidation state.

Far Infrared

The far infrared spectra of the chromate and dichromate were somewhat similar in number and shape of absorbance bands, but their locations were different. Sodium dichromate had absorbances at 475, 415, 380, 360, and 200 cm^{-1}; sodium chromate had absorbances at 475, 370, 350, and 190 cm^{-1}.

4.2.2.6 Nitrates

The nitrate-containing compounds studied were sodium and ammonium nitrates.

Mid Infrared

The two spectra were very similar, and the bonds due to the NO_3^{-1} ions were 2510, 1750, 1400, and 840 cm^{-1}. The only difference between sodium nitrate and ammonium nitrate was the absorbance between 3300 and 2800 cm^{-1}, which arose from N-H stretching modes.

Far Infrared

There were no differences between the far infrared spectra of sodium nitrate and ammonium nitrate.

4.2.2.7 Sulfate and Sulfite

The compounds used to draw comparisons between sulfate and sulfite ions were sodium sulfate and sodium sulfite.

Mid Infrared

Any mid infrared absorbance difference between the anions is due to the molecular structure. Sulfate anion has a tetrahedral structure where sulfite has a pyramidal structure; their structural differences were observed in the mid infrared. Sodium sulfate had major absorbances at 1100, 640, and 620 cm^{-1}; sodium sulfite had major absorbances at 900, 630, and 490 cm^{-1}. The identification of a sulfate-containing compound compared to a sulfite by infrared was straightforward.

Far Infrared

The comparison between sodium sulfate and sodium sulfite in the far infrared was just as straightforward as the comparisons in the mid infrared. Again, because the molecular structure was different, the bonding between

metal and anion were different. The differences in bonding were observed as lattice bond vibrations in the far infrared. Sodium sulfate had two main absorbances, a broad absorbance at 210 cm^{-1} and a second at 140 cm^{-1}. Sodium sulfite had two sharp absorbances at 225 cm^{-1} and 175 cm^{-1}.

4.2.2.8 Nitrate and Nitrite

The compounds used to draw comparisons between nitrate and nitrite ions were sodium nitrate and sodium nitrite.

Mid Infrared

As in the case of sulfate and sulfite, nitrate and nitrite had different mid infrared spectra. The bonding difference between nitrate and nitrite was similar because both had the potential to form bidentate radicals. The difference in the infrared spectra was a shift in the wavelength of the absorbances. Sodium nitrate had absorbances at 2510, 1750, 1400, and 840 cm^{-1}; sodium nitrite had absorbances at 1300 and 810 cm^{-1}. Mid infrared distinguished between nitrate and nitrite.

Far Infrared

The far infrared spectra of sodium nitrate and sodium nitrite were very similar. The nitrate and nitrite anions did not have any major absorbances in the far infrared region.

4.3 SUBTASK 3 - DETERMINE WHETHER THE 400 TO 100 cm^{-1} REGION IS INDEPENDENT OF INCLUDED WATER

The far infrared spectra of inorganic compounds are greatly affected by the presence of water. Water alters the spectrum because the crystal structure of the compound changes from one form to another, depending on the extent of water of hydration. To illustrate this point, the far infrared spectrum of calcium sulfate was acquired under various conditions. Water in calcium sulfate has the following three configurations:

$CaSO_4 \cdot 2\ H_2O$	dihydrate
$CaSO_4 \cdot 1/2\ H_2O$	hemihydrate
$CaSO_4$	anhydrous

An experiment was conducted to obtain the far infrared spectra of calcium sulfate in the dihydrate state. This sample was then heated to drive off the water of hydration; the anhydrous state of calcium sulfate was obtained and its spectrum recorded. The far infrared spectra of the dihydrate and anhydrous calcium sulfate were compared and changes were attributed to the presence of water.

The far infrared spectrum of calcium sulfate dihydrate is shown in Figure 2. The major absorbances were at 230, 210, and 120 cm^{-1}. The crosses on Figure 2 indicate absorbances steming from the presence of atmospheric water. The far infrared calcium sulfate spectrum in the anhydrous state is shown in Figure 3. The major absorbances were at 250-275, 190, and 170 cm^{-1}. Comparison of the spectra in Figures 2 and 3 reveals pronounced differences exist. The observed differences in the far infrared region result from changes in structure of interactions with the infrared action bonding modes caused by the presence of water in the sample. This experiment also demonstrated another concern for the use of infrared spectroscopy for inorganic speciation in the far infrared range. Namely, special sample handling techniques have to be employed in order to maintain a consistence in acquiring spectra because of the effects of water in the 300 to 100 cm^{-1} frequency range and the experimental method used to obtain spectra. Much of the work reported here was accomplished in a single-beam mode in which the optical compartment has been purged with non-infrared active gas to remove atmospheric water and carbon dioxide.

The calcium sulfate experiment also showed the effect of atmospheric water present in the optical path in the far infrared region; Figure 2 has crosses on it where absorbances were due to atmospheric water. In order to assess this atmospheric water effect, a series of experiments were performed. First, far infrared spectrum of air in the spectrometer was obtained. The spectrum of air showed where water absorbed in the far infrared region. Next, a spectrum of a compound was obtained in the same environment as the air sample; finally, the spectrometer was purged with zero air. Zero air is the term used for air which was free from infrared active in purities, such as H_2O and CO_2. The purge removed atmospheric water and a spectrum of the same compound was obtained in a water-free environment.

The far infrared spectrum of a low concentration of atmospheric water in air in the spectrometer's optical is shown in Figure 4. The major absorbances of atmospheric water were at 280-276, 155-148, 141-133, 124-120, and 107-100 cm^{-1}. These absorbances are often shown as blank areas in the spectrum. The blank areas are produced by the instrument plotter; existing computer software in the Digilab 15-C instrument instructs the plotter not to plot narrow, intense absorbances, (e.g., the pen is lifted from the recording paper when large absorbances due to water are encountered). The Digilab software distinguishes between a very intense narrow band and a strong absorbance band.

A far infrared spectrum of anhydrous calcium sulfate was obtained in the same environment as the air and is shown in Figure 5.1. Again, blank areas appeared in the calcium sulfate spectrum at 177, 170, 155-149, 140, 130, 126-120, and 110-100 cm^{-1}, these match up with the major and minor atmospheric water absorbances. Also, the sharp absorbances at 270 and 255 cm^{-1} matched up with the water absorbances.

Next, a zero air purge was employed to remove the atmospheric water from the spectrometer. Figure 5.2 is a spectrum of the same calcium sulfate sample with purge on for 42 minutes. The purge had a direct affect on atmospheric

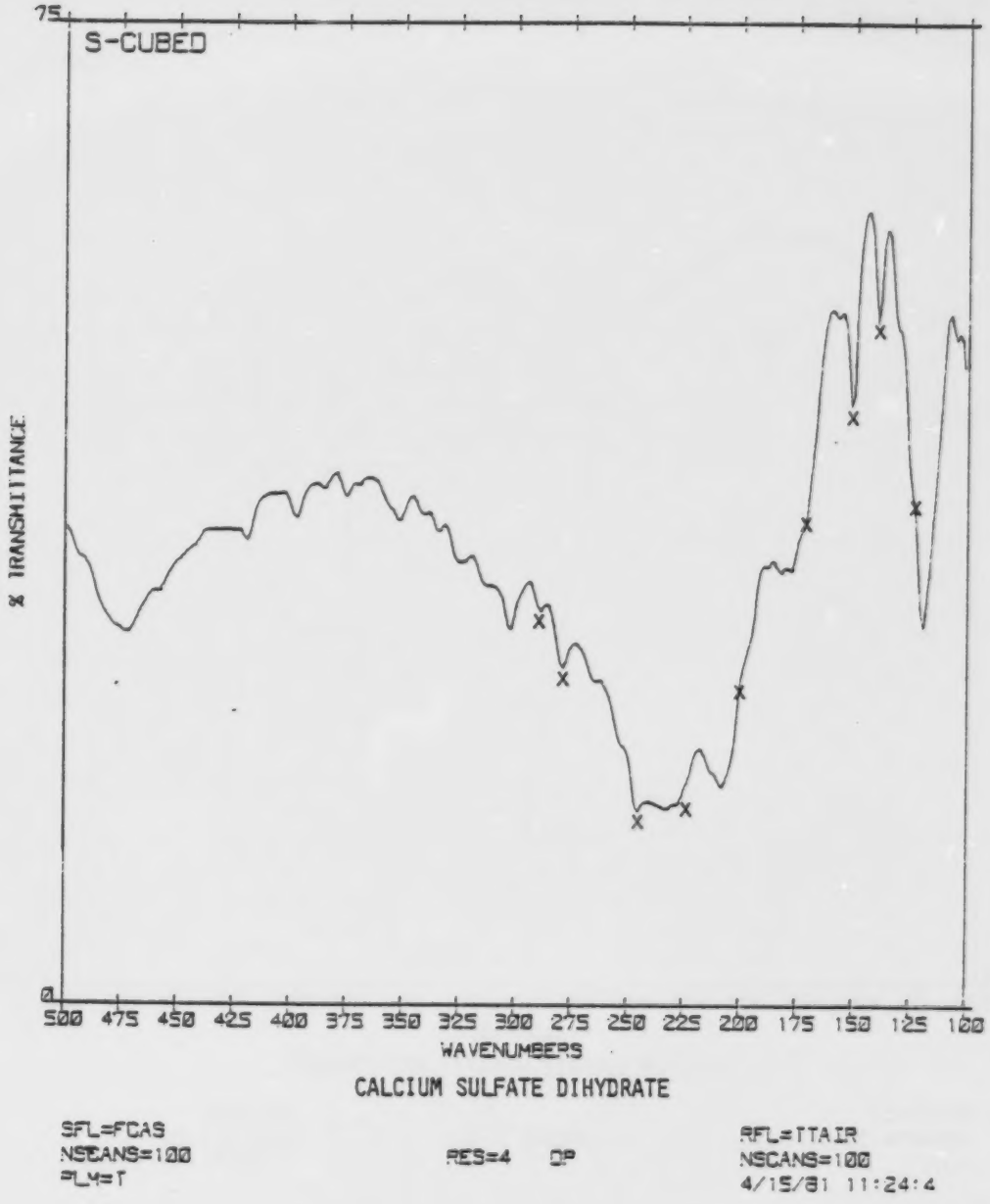


Figure 2. Far Infrared Spectrum of Calcium Sulfate Dihydrate

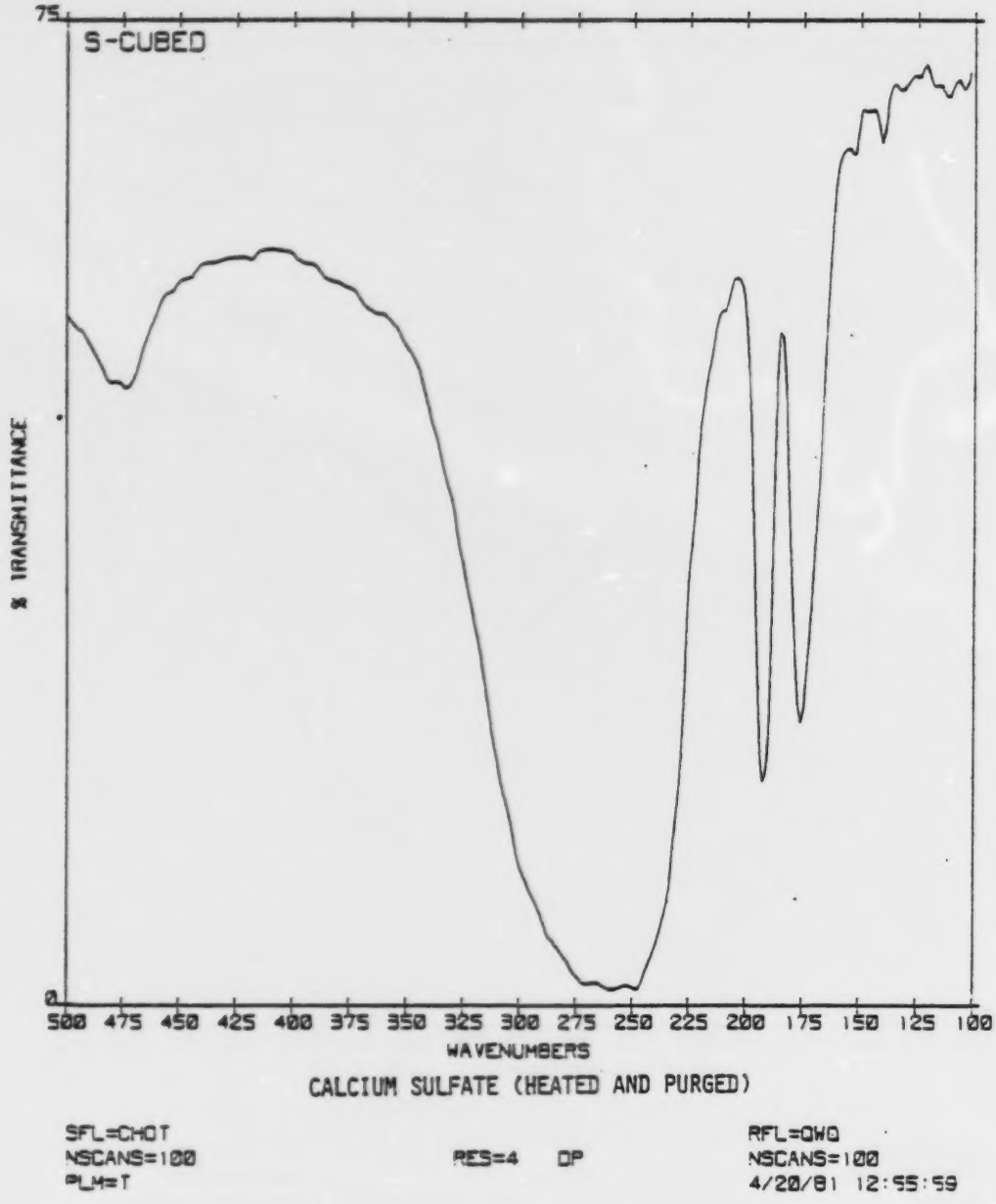


Figure 3. Far Infrared Spectrum of Anhydrous Calcium Sulfate

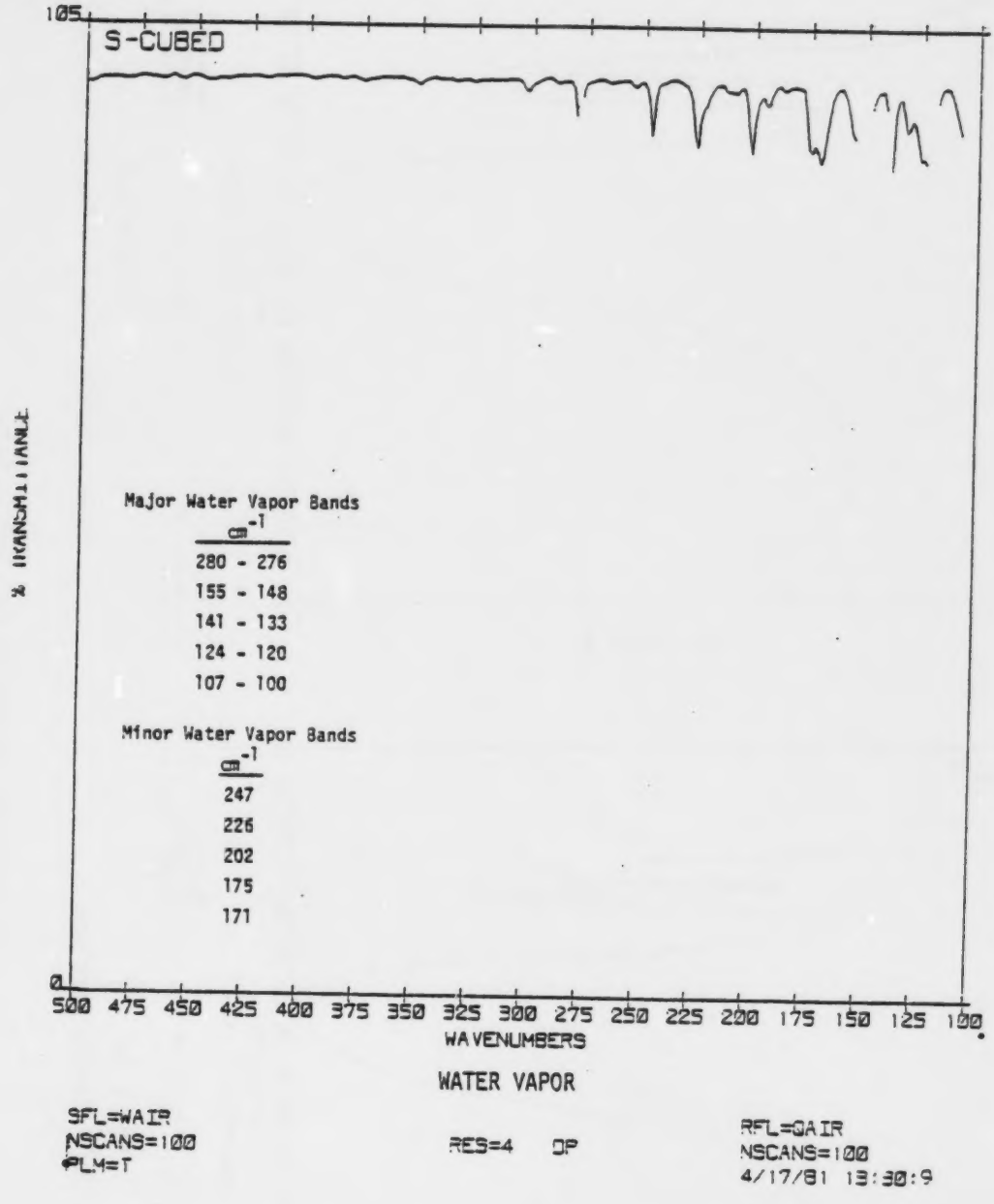


Figure 4. Far Infrared Spectrum of Water Vapor

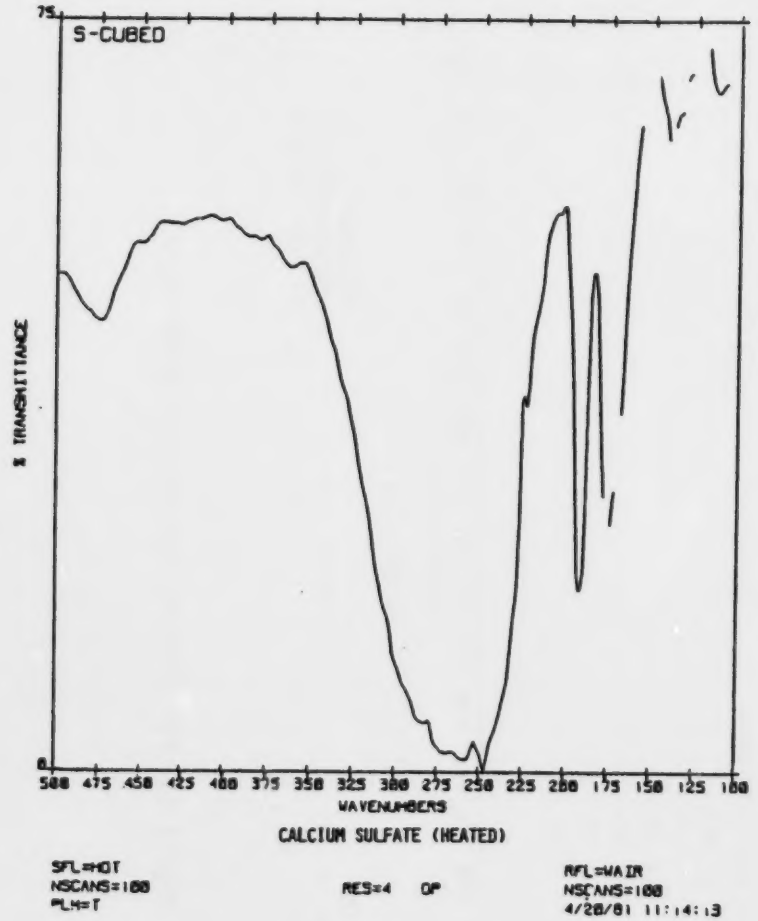


Figure 5.1

Heated KBr - Sample Specimen

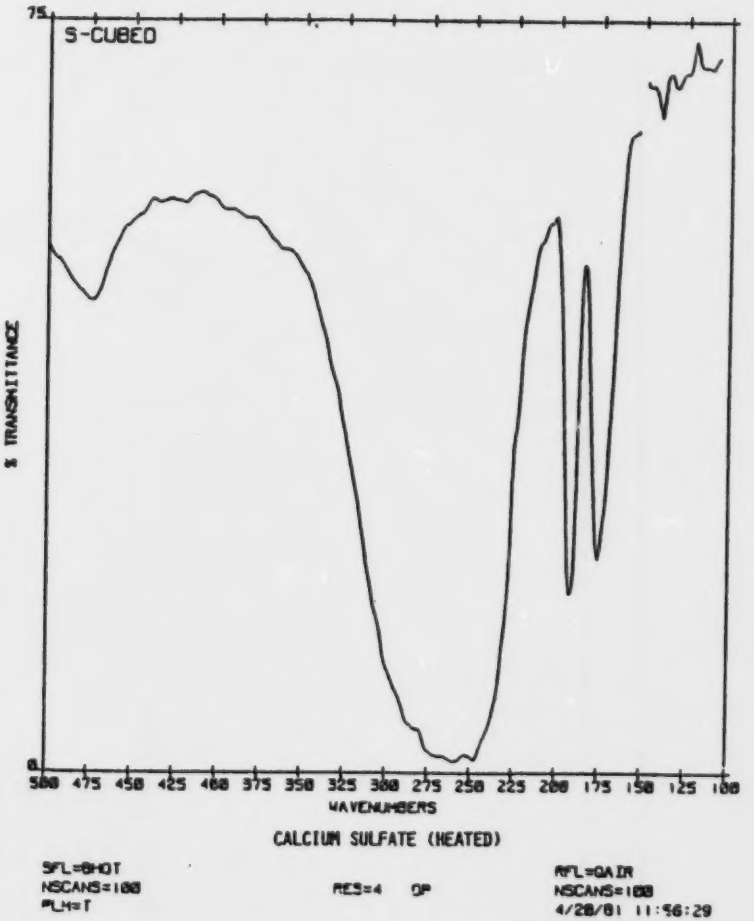


Figure 5.2

Heated Sample Plus 42 Minutes Zero Air Purge

Far Infrared Spectra of Calcium Sulfate

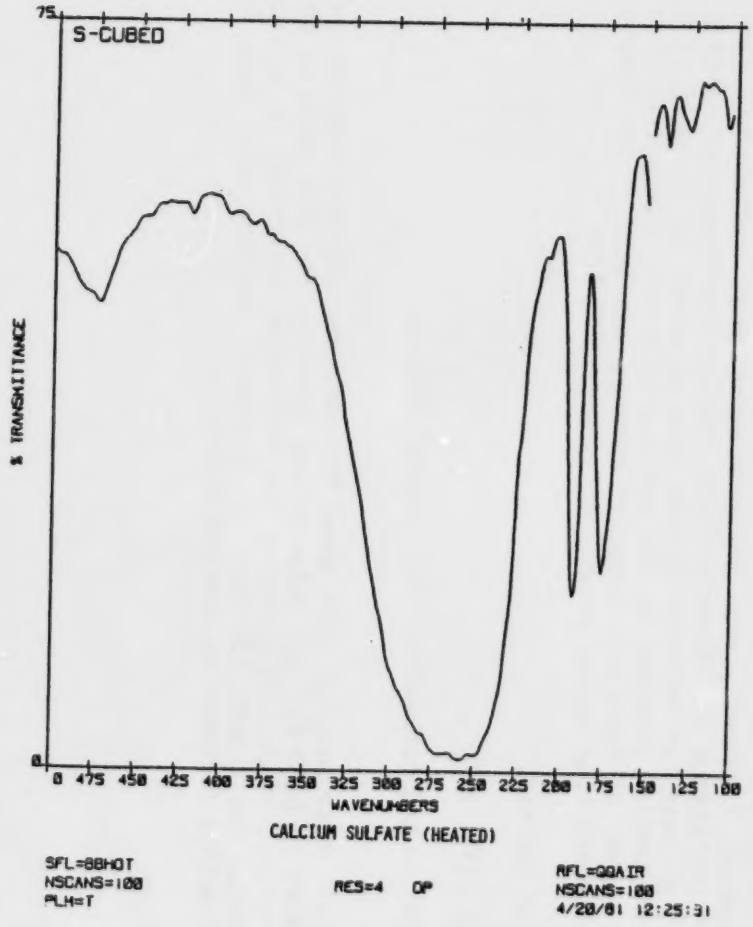


Figure 5.3
Heated Sample Plus 71 Minutes Zero Air Purge

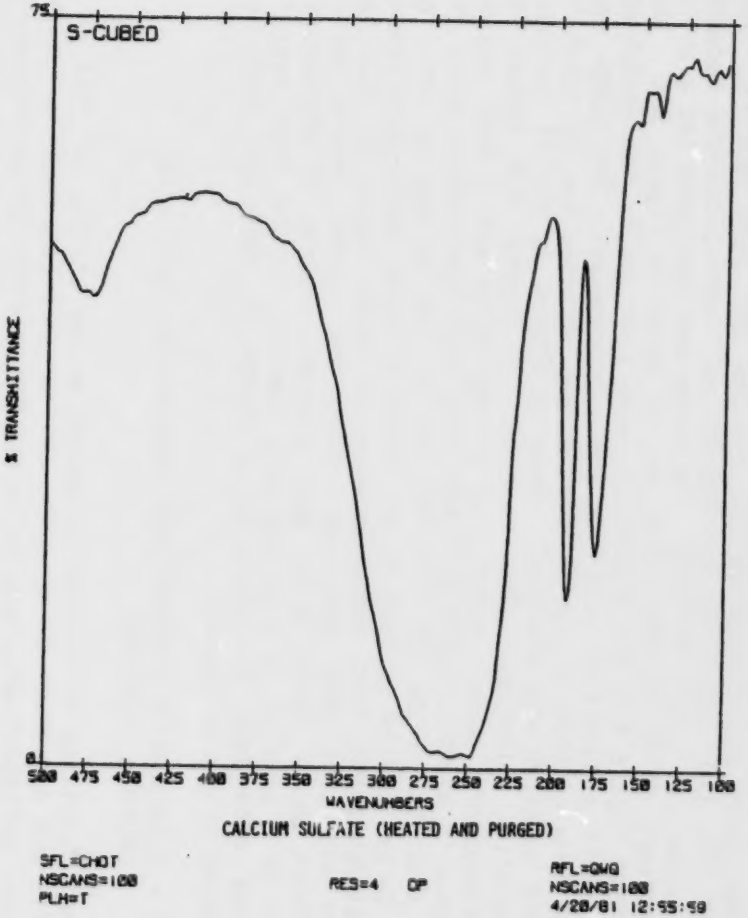


Figure 5.4
Heated Sample Plus 106 Minutes Zero Air Purge

Far Infrared Spectra of Salcium Sulfate

water because the sharp absorbances at 270 and 255 cm^{-1} were removed. The blank regions at 177, 170, 140, 130, and 126-120 cm^{-1} were plottable because the atmospheric water was slowly removed. The purge was continued and a third spectrum was obtained at 29 minutes later and is shown in Figure 5.3. The differences between Figure 5.2 and Figure 5.3 were very small, but indicated that there was still atmospheric water in the spectrometer. The purge was continued for 35 more minutes, a fourth spectrum was obtained and is shown in Figure 5.4. This spectrum was previously shown as Figure 3, but is included here for comparative purposes. The spectrum in Figure 5.4 showed no indication of atmospheric water; total time of the purge was 1 hour and 46 minutes. The results of this experiment indicated that atmospheric water did affect spectra obtained in the far infrared region, but no special sampling techniques had to be applied as long as the specific water bands were known. One simple distinguishing fact about atmospheric water bands in the far infrared region was that they were very sharp and narrow, where normal infrared absorbance bands tended to be much broader. Again, if atmospheric water tended to be a problem in distinguishing spectra, it was very easy to repeat the above experiment by employing a purge of zero air into the spectrometer during sample collection.

4.4 SUBTASK 4 - CHARACTERIZE ENVIRONMENTAL SAMPLES FOR TRACE LEVEL CHEMICAL COMPOUNDS

This effort consisted of studies to determine the utility of FTIR as a means to identify and determine the quantity of inorganic compounds in typical particulate matter pollutant emissions collected during other EPA environmental assessment studies. This subtask is closely related to the next two subtasks dealing with (1) matrix isolation studies using FTIR spectral subtraction methods and chemical treatment, and (2) attenuated total reflectance (ATR) methodology for assistance in characterizing complex environmental samples. In this subtask, mid and far infrared spectra were obtained for three environmental assessment samples provided by EPA and a preliminary interpretation of the spectra in terms of inorganic compound species was made. The samples examined were obtained from ducted gaseous emissions taken from

- A copper smelter,
- A steel mill, and
- A fluidized bed combustion (FBC) control process.

Portions of these samples were used for infrared characterization and they were prepared in both KBr and polyethylene matrices for mid infrared and far infrared regions, respectively, using the techniques described in Section 4.2. In general, the identifications of inorganic species were made by comparison with active frequencies shown in Figure 1.

4.4.1 Copper Smelter Sample

The mid infrared spectrum of the particulate matter collected at the copper smelter, shown in Figure 6, indicates the presence of sulfate at 1100 cm^{-1}, possibly a halogen at 600 cm^{-1}, and water at 3500 and 1600 cm^{-1}. The far infrared spectrum, Figure 7, shows the presence of arsenic (III) oxide. The sample spectrum was almost identical to the reference spectrum of arsenic (III) oxide (Figure A-5b, Appendix A). With almost a positive identification of arsenic (III) oxide from the far infrared spectrum, the reference mid infrared spectrum was compared to the mid infrared spectrum of the sample. The sample spectrum compared well with the mid infrared reference spectrum of arsenic (III) oxide. Also, the mid infrared spectrum suggested the additional presence of sulfate at 1100 cm^{-1} bands.

4.4.2 Steel Mill Sample

The mid infrared spectrum of the steel mill sample collected in the electrostatic precipitator (ESP) is shown in Figure 8. The spectrum shows the presence of nitrate or ammonium at 1400 cm^{-1} and sulfate or silicate at 1100 cm^{-1}. The far infrared spectrum (Figure 9) did not provide any useful information.

4.4.3 FBC Sample

The mid infrared spectrum of the FBC sample is shown in Figure 10. The spectrum indicated the presence of sulfate and/or silicate at 1100 cm^{-1}. A comparison between the mid infrared spectrum of the FBC sample and a reference calcium sulfate dihydrate spectrum (Figure 2) showed similarities at 3550, 3400, 1100, 650, 600, and 450 cm^{-1}. The far infrared spectrum (Figure 11) did not provide any supplemental information.

4.5 SUBTASK 5 - ELIMINATION OF SAMPLE MATRIX EFFECTS

The environmental samples examined in Subtask 4 were investigated using two alternative means to eliminate the matrix effects on the resulting spectra. The first technique consists of a spectral subtraction method in which the spectra of an identified constituent in the sample are electronically subtracted from the spectra of the sample. In general, this method is very good at identifying small differences between sample and matrix spectra, which otherwise cannot be readily discerned. This is one of the strong advantages of the use of FTIR for characterization of unknown samples.

In this procedure, some knowledge is required of the sample so that candidate matrix materials can be selected for study. The intensity of the subtracted spectra must also be selected, somewhat by guesswork for the initial selection, using some of the clearly identified stronger absorption bands in the candidate matrix material spectra as the reference point for implementing the electronic subtraction. In some cases, when the sample

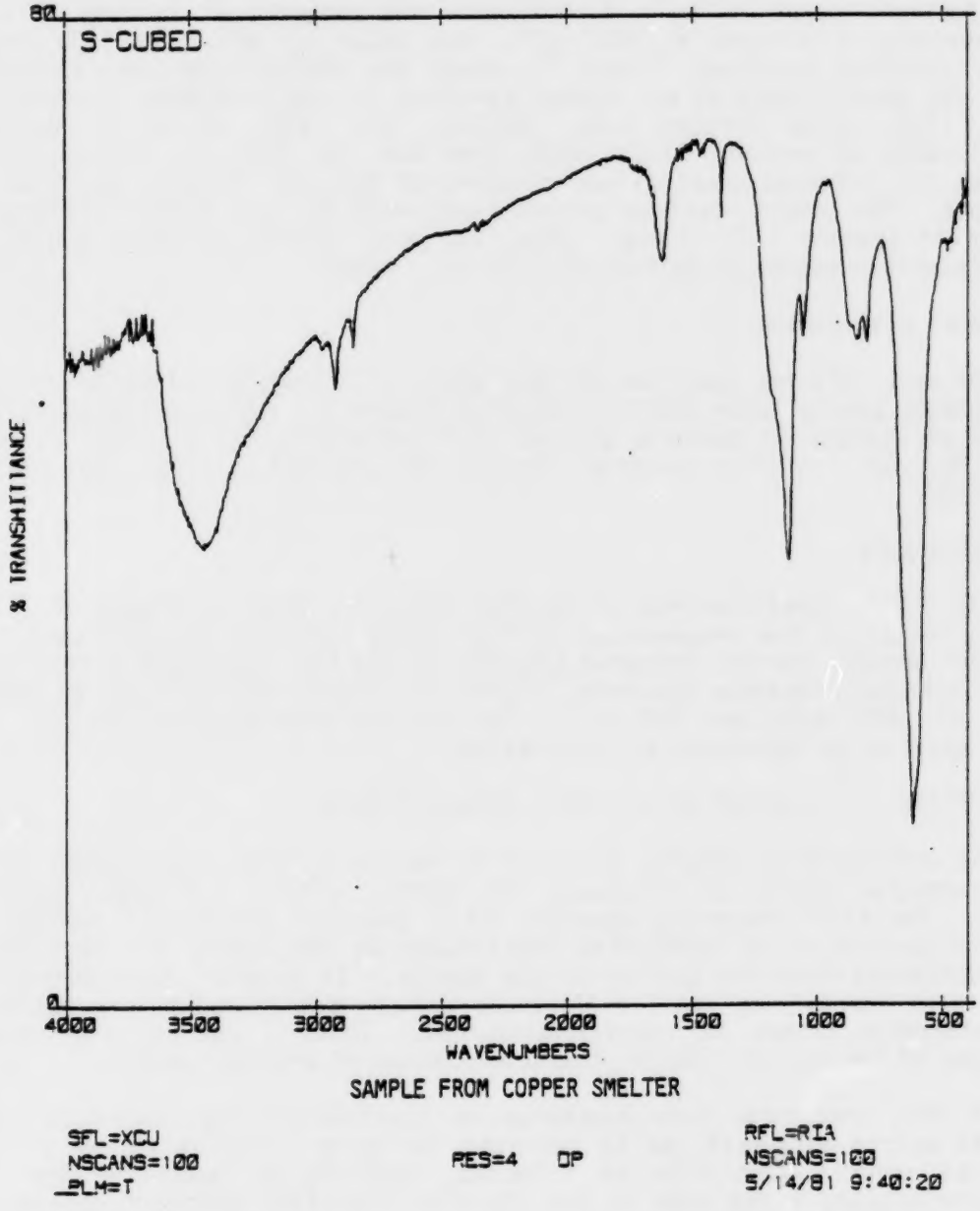


Figure 6. Mid Infrared Spectrum of Copper Smelter Emissions

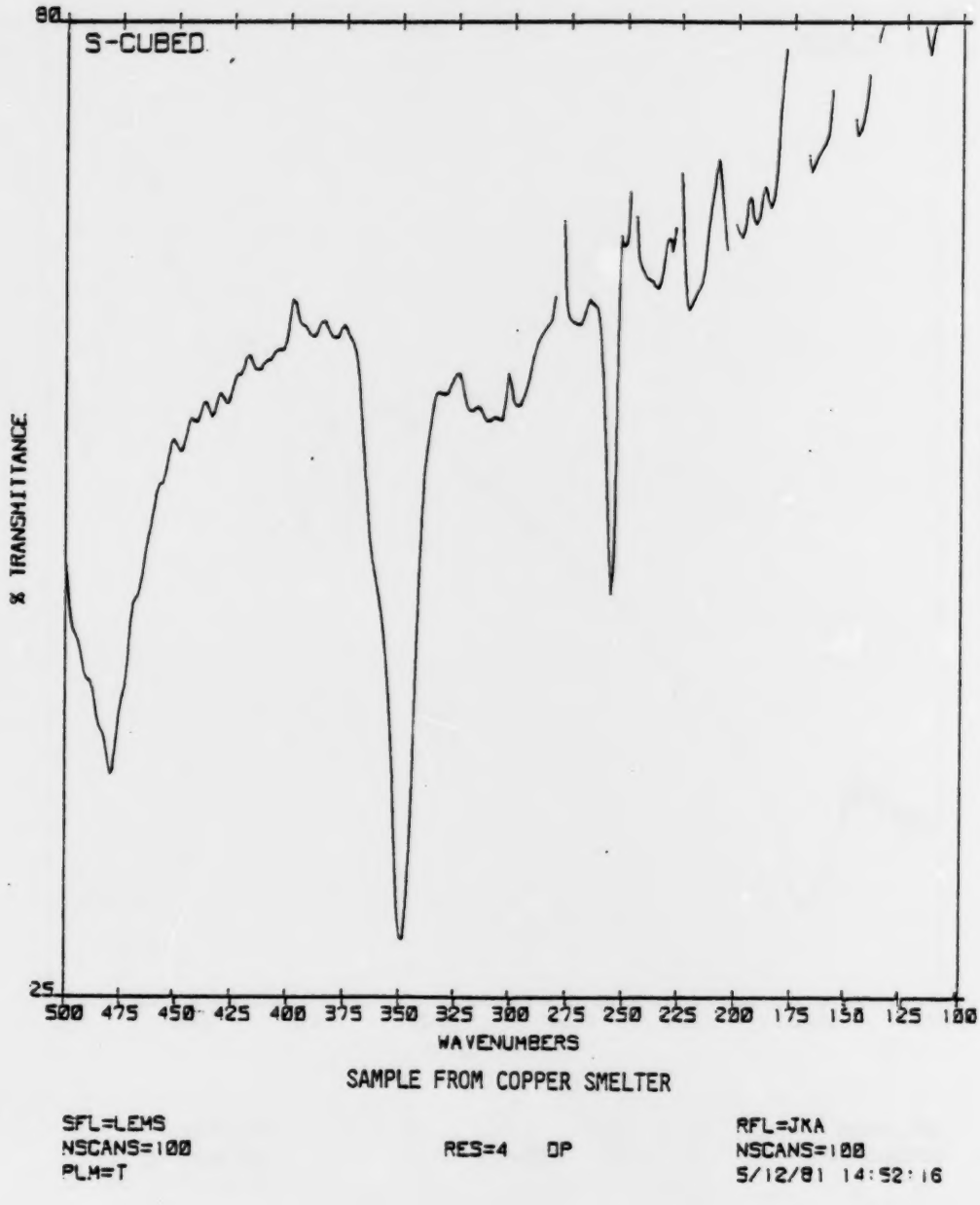


Figure 7. Far Infrared Spectrum of Copper Smelter Emissions

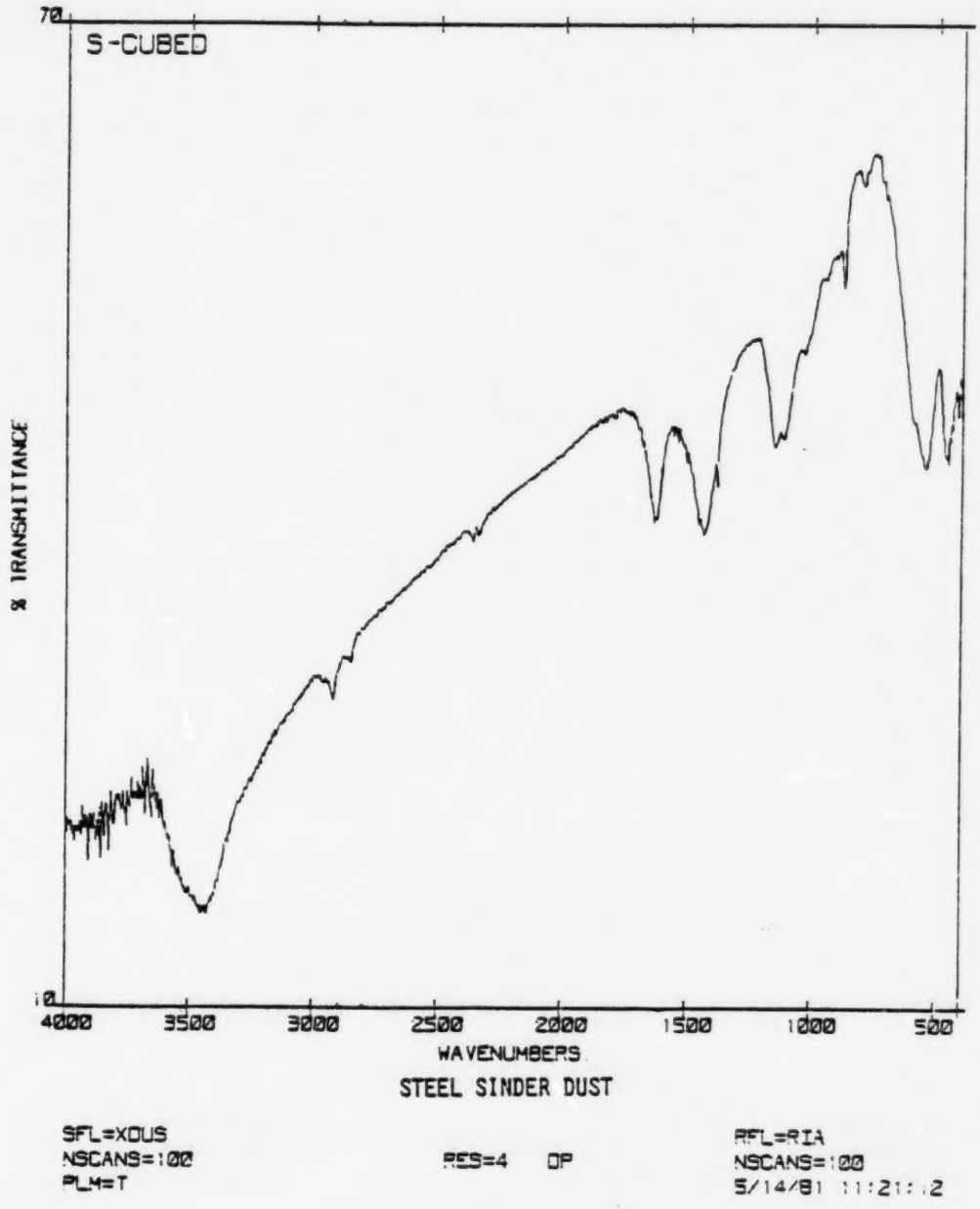


Figure 8. Mid Infrared Spectrum of Steel Mill Emissions (Collected in ESP)

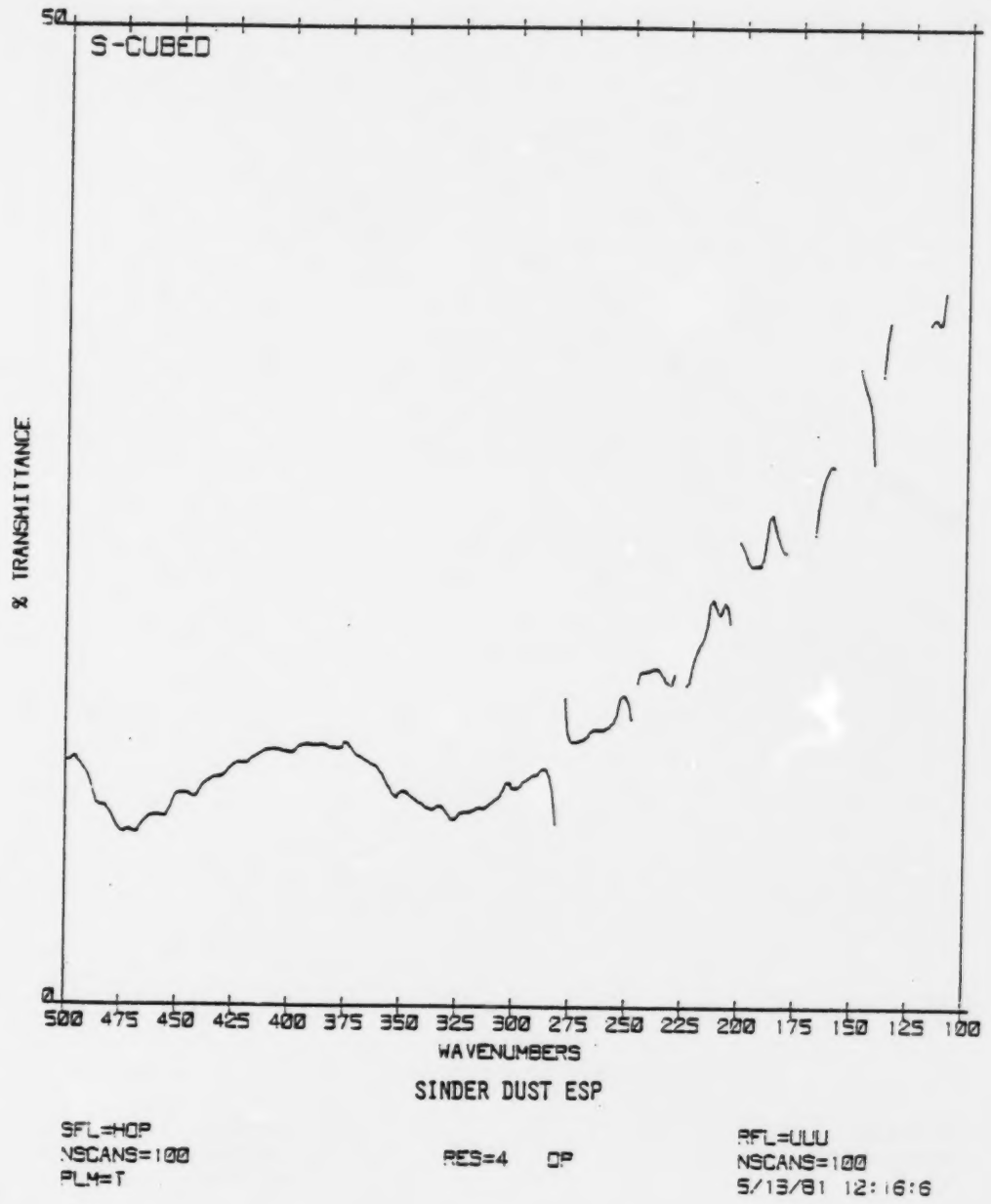


Figure 9. Far Infrared Spectrum of Steel Mill Emissions (Collected in ESP)

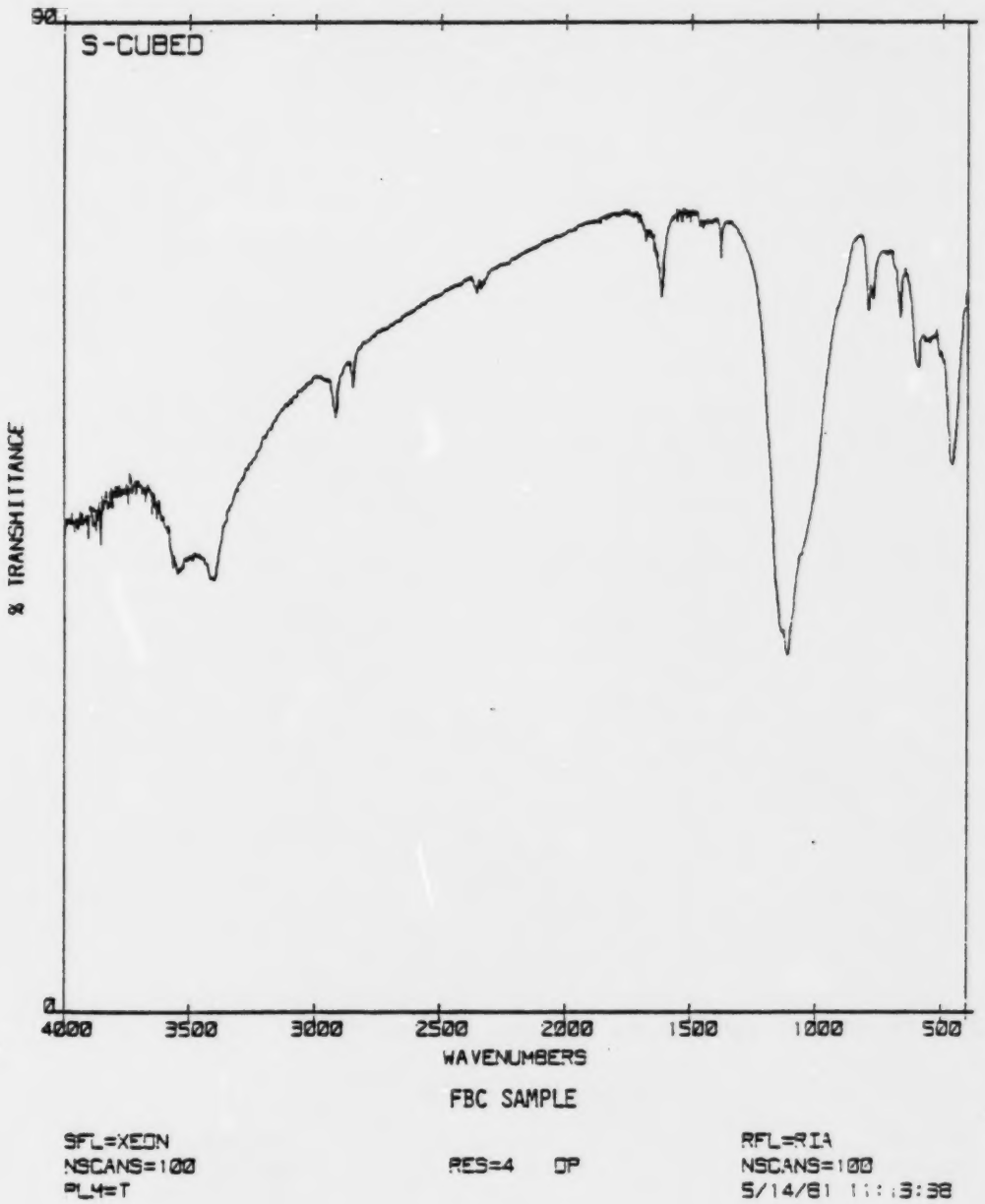


Figure 10. Mid-Infrared Spectrum of FBC Emissions

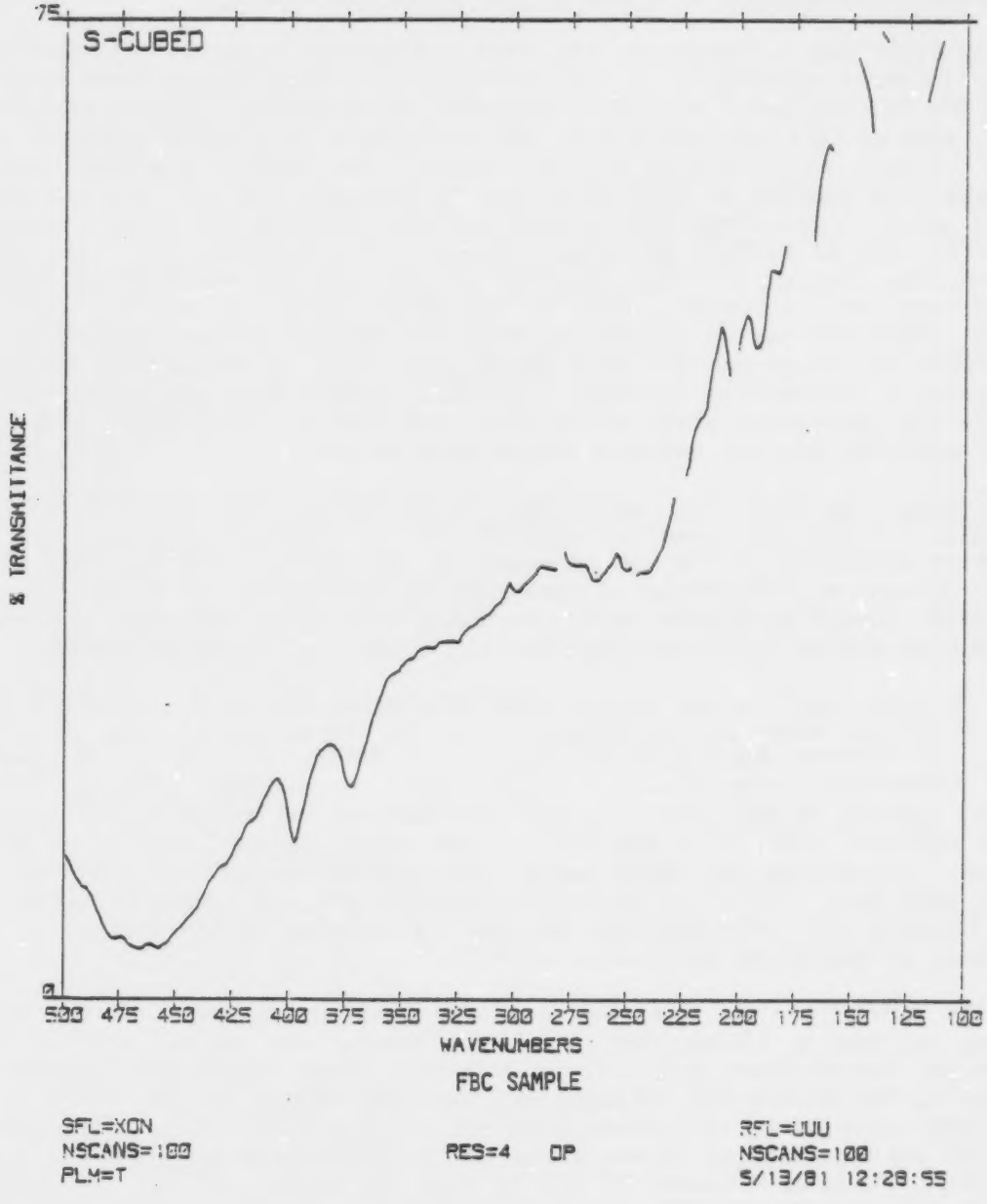


Figure 11. Far Infrared Spectrum of FBC Emissions

spectrum provides very little information, spectral subtraction cannot be utilized readily. With the environmental samples studied in this task, the copper smelter sample was positively identified as arsenic (III) oxide without the use of spectral subtraction. The spectra of the other two samples were too general for ready use of spectral subtraction methodology.

As described in Subtask 3, atmospheric water was shown to interfere with the far infrared spectrum of calcium sulfate. The long purging time required by the Digilab equipment made this procedure non-practical. Newer instrumentation, such as that now provided by IBM Instruments in which the optical path can be located, would eliminate this problem. The initial approach used to eliminate this problem in this study was to subtract the air spectrum (containing water vapor) from the calcium sulfate spectrum and obtain a water vapor-free calcium sulfate spectrum. However, this approach was found to be not practical because (1) the spectrum of air and the spectrum of calcium sulfate were very different, and (2) the water bands in the air were too intense, and could not be subtracted from the calcium sulfate spectrum. The differences in intensity and band shape gave rise to misleading and non-interpretable subtraction spectra. Spectral subtraction was found to be possible for absorbance bands which were less than 0.8 absorbance units and where comparable matrices and band shapes were present.

Another approach for assisting in isolating the spectrum of the pollutants in the environmental samples was by chemical treatment of the samples to solubilize either the pollutant or the matrix. The key step is to archive selective differences between the solubilization of either of the components. Leaching studies were undertaken with water and acid separately to determine whether sufficient differential solubilization was achieved.

The water leaching was accomplished by placing 100 mg of the sample in 5 mL of distilled water and continued mixing for three hours. The resulting mixture was filtered and the filter residue was dried. The residue was placed in the appropriate infrared matrix and its spectrum recorded. Figures 12a-14a show the spectra of the dried residue from each of the environmental samples (copper smelter, steel mill and FBC cyclone catch, respectively) after water leaching. Neglecting the water bands, the residue spectra of each of the samples were very similar to their corresponding original spectra; hence, the water leaching did not cause the desired differential solubilization of the pollutants or background matrix.

The acid leaching technique was very similar to that of the water leaching in that a 100-mg portion of the sample was treated with a 5-mL portion of concentrated hydrochloric acid for three hours with agitation. Once again, the mixture was filtered and then the residue on the filter paper was washed three times with 25-mL portions of distilled water. The residue was dried and a portion of it was placed in an appropriate infrared matrix and a spectrum recorded. Figures 15 and 16 show the spectra of the dry residue from the acid digestion of the steel mill samples, and Figures 15 and 16 show

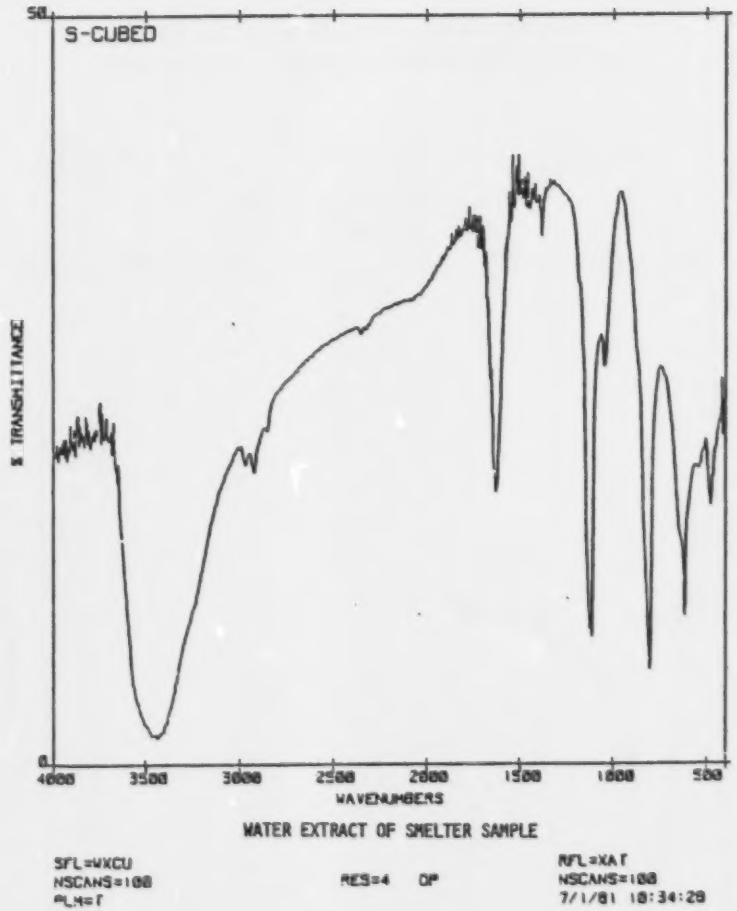


Figure 12a. Mid Infrared Spectrum of Smelter Emissions Water Extract

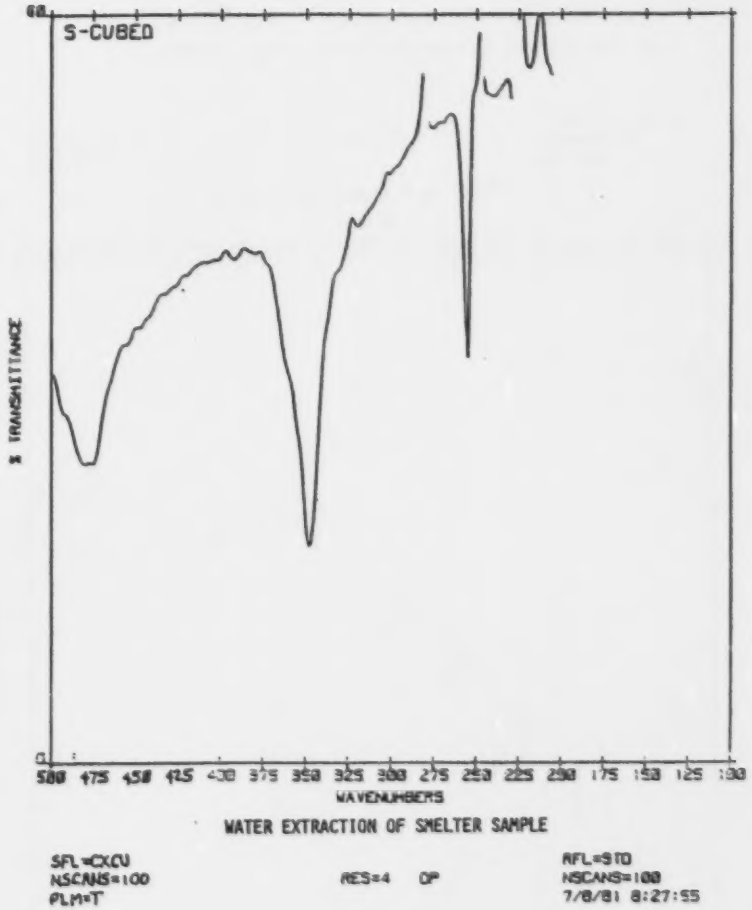


Figure 12b. Far Infrared Spectrum of Smelter Emissions Water Extract

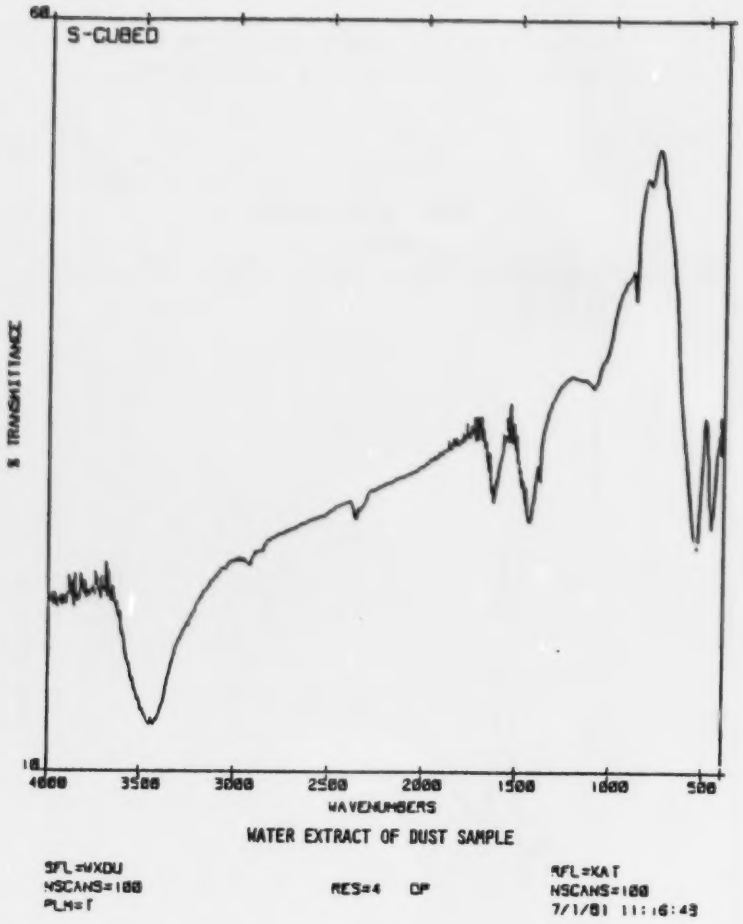


Figure 13a. Mid Infrared Spectrum of Steel Mill Emissions Water Extract

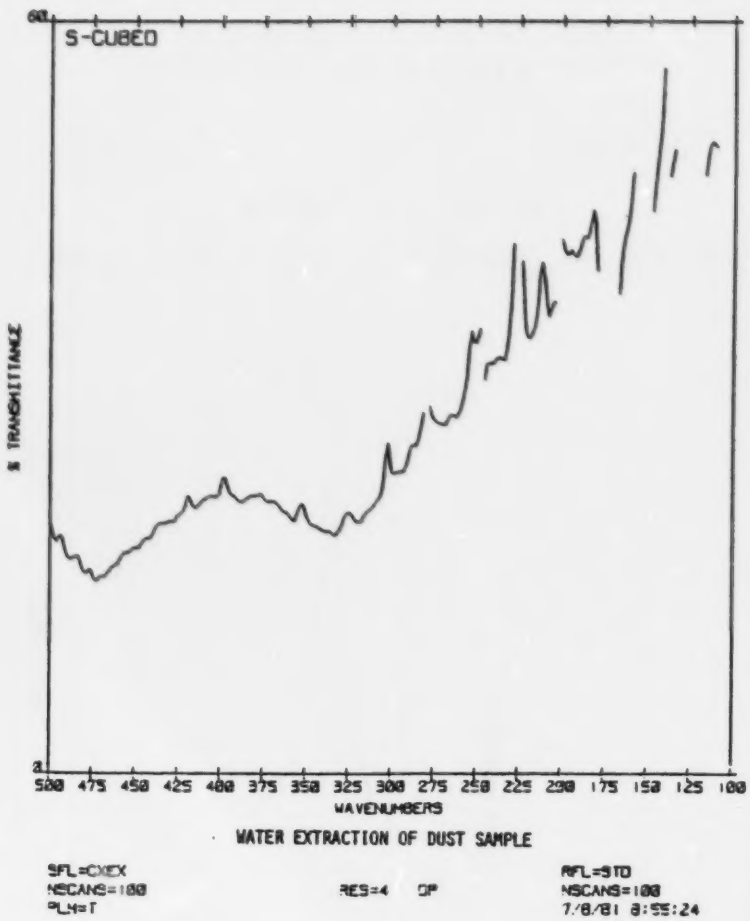


Figure 13b. Far Infrared Spectrum of Steel Mill Enissions Water Extract

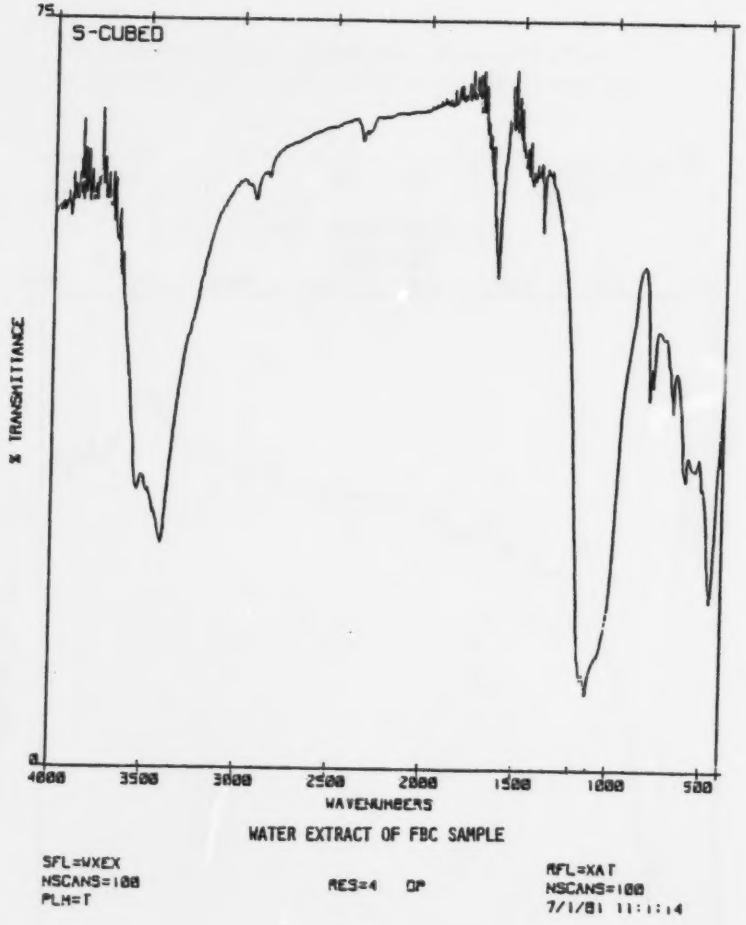


Figure 14a. Mid Infrared Spectrum of FBC Emissions Water Extract

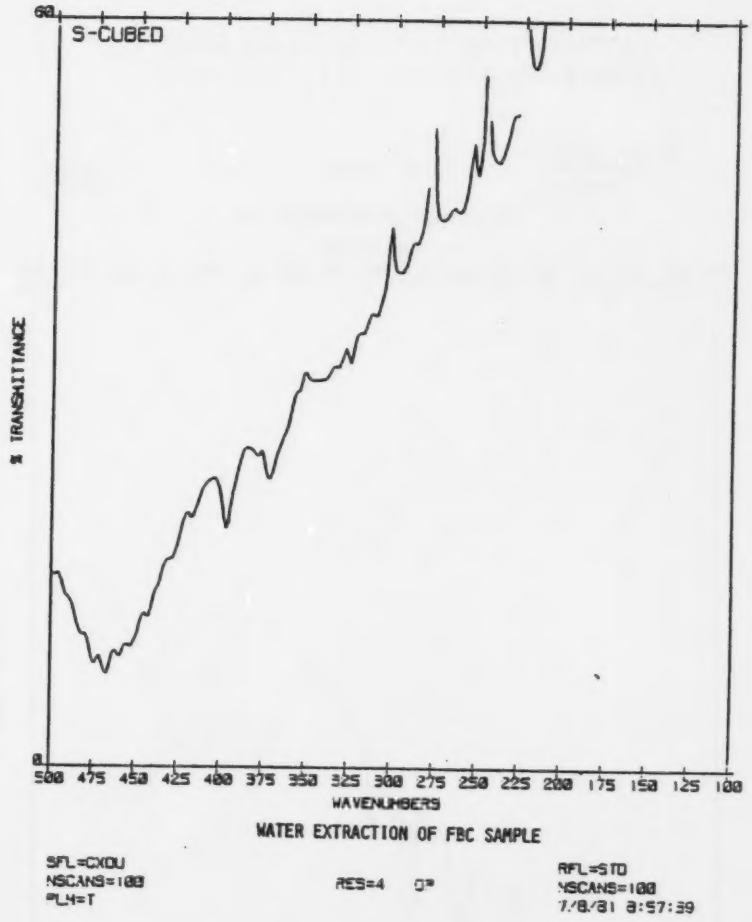


Figure 14b. Far Infrared Spectrum of FBC Emissions Water Extract

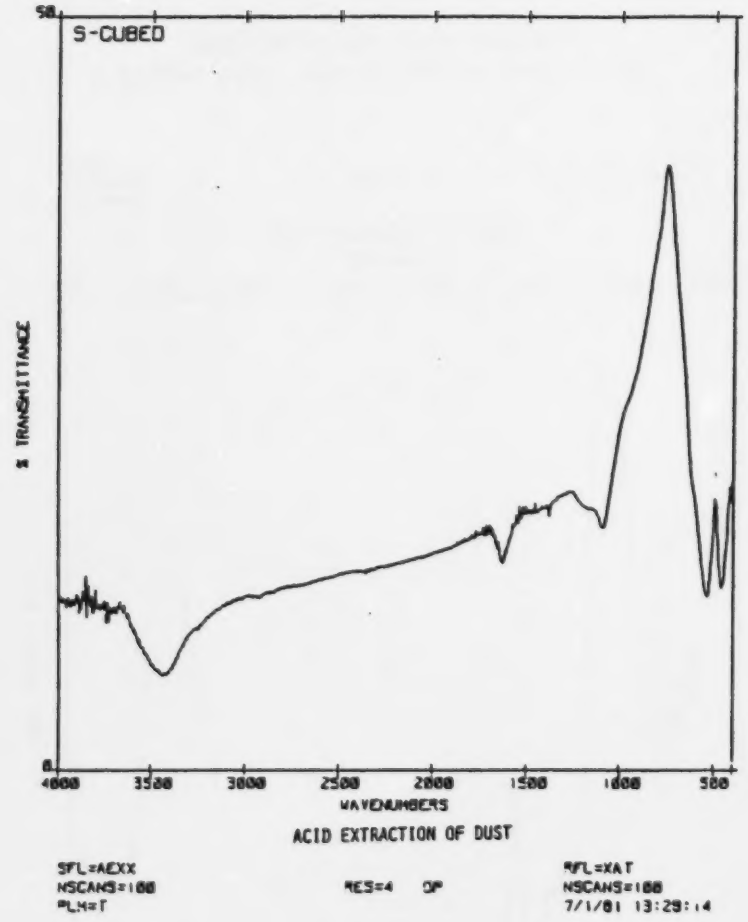


Figure 15a. Mid Infrared Spectrum of Steel Mill Emissions Acid Extract

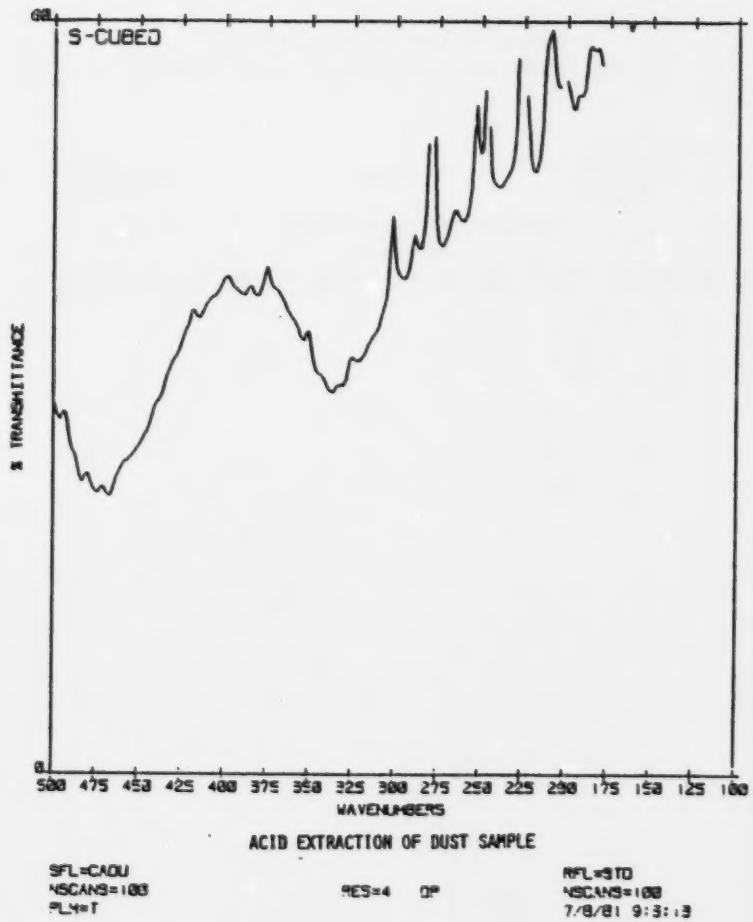


Figure 15b. Far Infrared Spectrum of Steel Mill Emissions Acid Extract

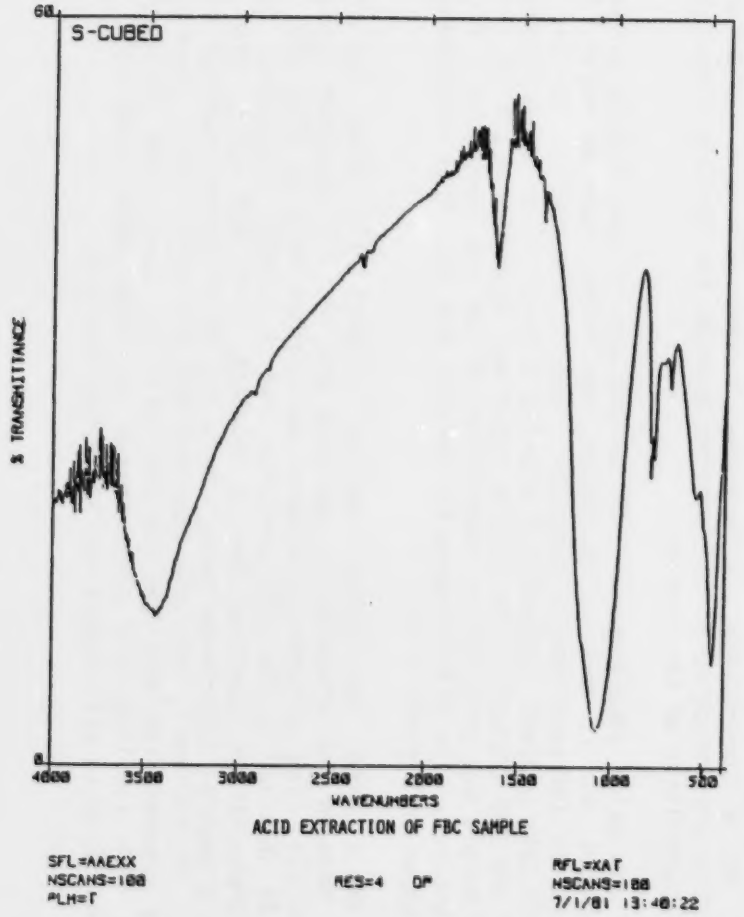


Figure 16a. Mid Infrared Spectrum of FBC Emissions Acid Extract

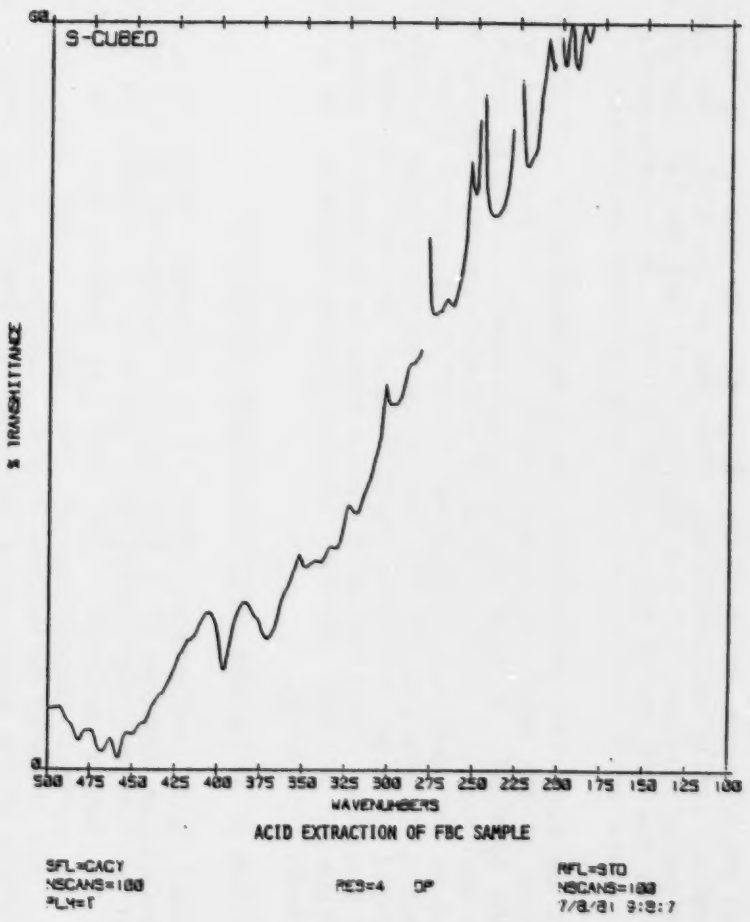


Figure 16b. Far Infrared Spectrum of FBC Emissions Acid Extract

the spectra of the acid extraction of the FBC particulate sample. As expected, the copper smelter sample was completely dissolved by the acid. The spectra of the acid digested residues for both the steel mill and the FBC samples were very similar to the spectra of the original samples. As a consequence, the acid extraction did not provide any help in characterizing the unknown.

Without any supporting information from water leaching or acid digestion, characterization of the sample background matrix from the steel mill and FBC sample was not possible. Without the background matrix, spectral subtraction could not be employed and identification of the environmental samples had to be made based on the combined pollutant-matrix infrared spectra alone. Based on these spectra, it appeared the FBC sample was mostly calcium sulfate from the mid infrared spectrum, but this identification was not confirmed by the far infrared spectrum. The steel mill sample appeared to contain nitrates or ammonium sulfate and silicon; the far infrared spectra indicated the presence of ferric nitrate [$Fe(NO_3)_3$].

4.6 . UTILIZATION OF ATTENUATED TOTAL REFLECTANCE METHODOLOGY

Attenuated total reflectance (ATR) is a technique where an apparent infrared transmission spectrum of a bulk sample is obtained by the multiple reflection of an infrared light which only penetrates a fraction of a wavelength into the sample material. The resulting spectra are, in fact, a measure of the surface composition of the sample rather than the bulk composition. This infrared reflection is made possible by differences in the refractive indices of the sample and a KRS (thallium bromoiodide) crystal used to obtain the attenuated total reflectance spectra. Conventional transmission infrared spectroscopy is a technique which measures the bulk composition of the sample. As a consequence, differences between ATR and transmission infrared spectra are indicated of differences between the surface composition and the bulk composition of the sample.

One of the major advantages of ATR methodology is that sample preparation is minimized, and it does not introduce impurities, such as water, that may be present in infrared sample matrices. Sample preparation for the ATR experiments in this project consisted of placing a layer of powdered sample on each side of the KRS crystal. The sample layer was approximately 1-mm thick. The powdered sample was prepared by communition of the raw sample in a Wig-L-Bug for two minutes. The mid infrared ATR spectra for the three environmental samples are shown in Figures 17-19.

The sample from the copper smelter (Figure 17) also had many similarities between the transmission spectrum and the ATR spectrum (compare Figures 6 and 17). The differences between the spectra were at 800, 600, and 490 cm^{-1}. At 800 cm^{-1}, the ATR spectrum had a single absorbance band, where the transmission spectrum had a doublet. At 600 cm^{-1}, the ATR spectrum had a doublet absorbance band, where the transmission spectrum had a single band. At 490 cm^{-1}, the ATR spectrum had a single, sharp absorbance band and the transmission spectrum did not have any band. The differences between the ATR spectrum and transmission spectrum were clear-cut, but interpretation of these differences was not possible.

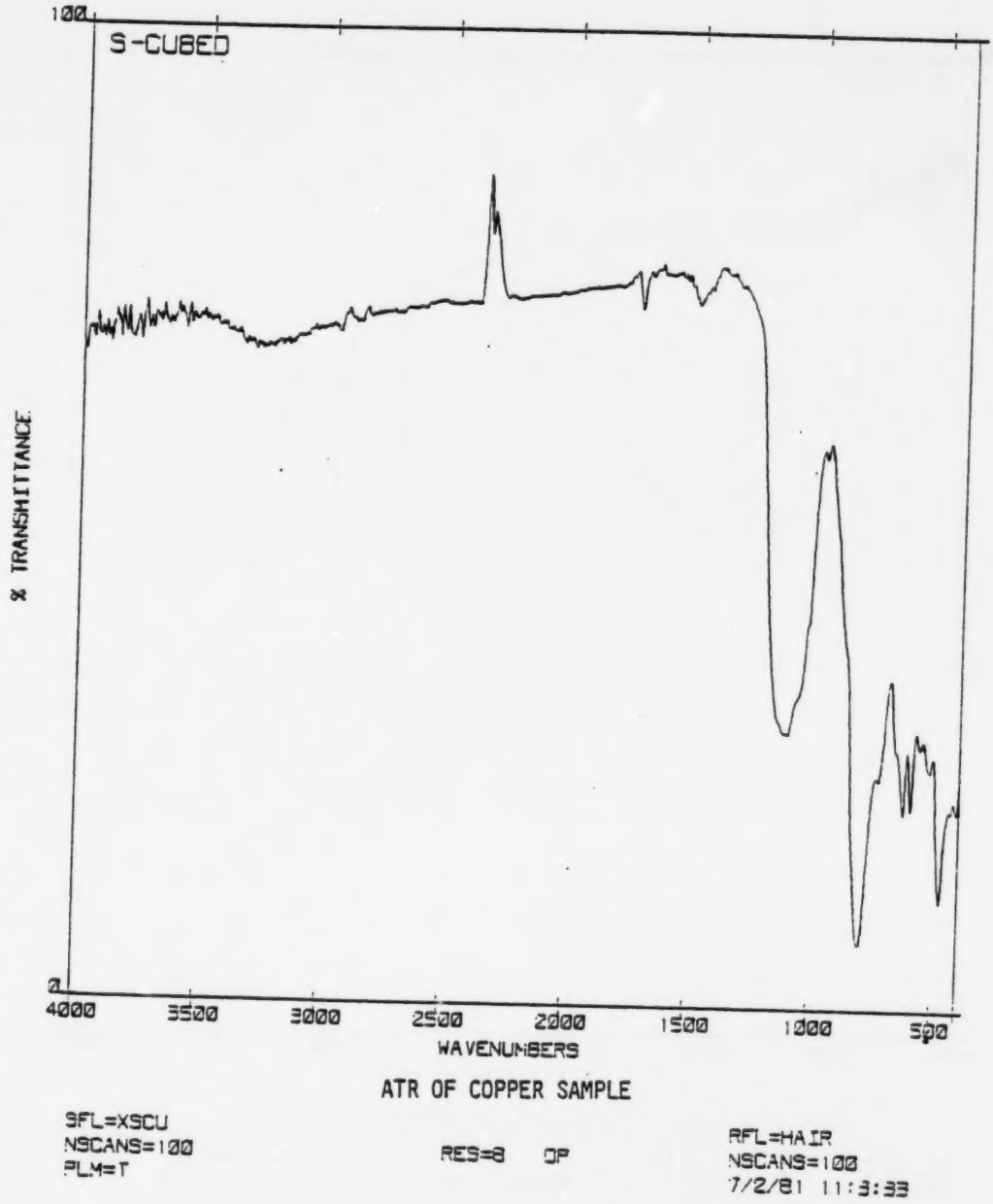


Figure 17. Mid Infrared ATR Spectrum of Copper Smelter Emissions

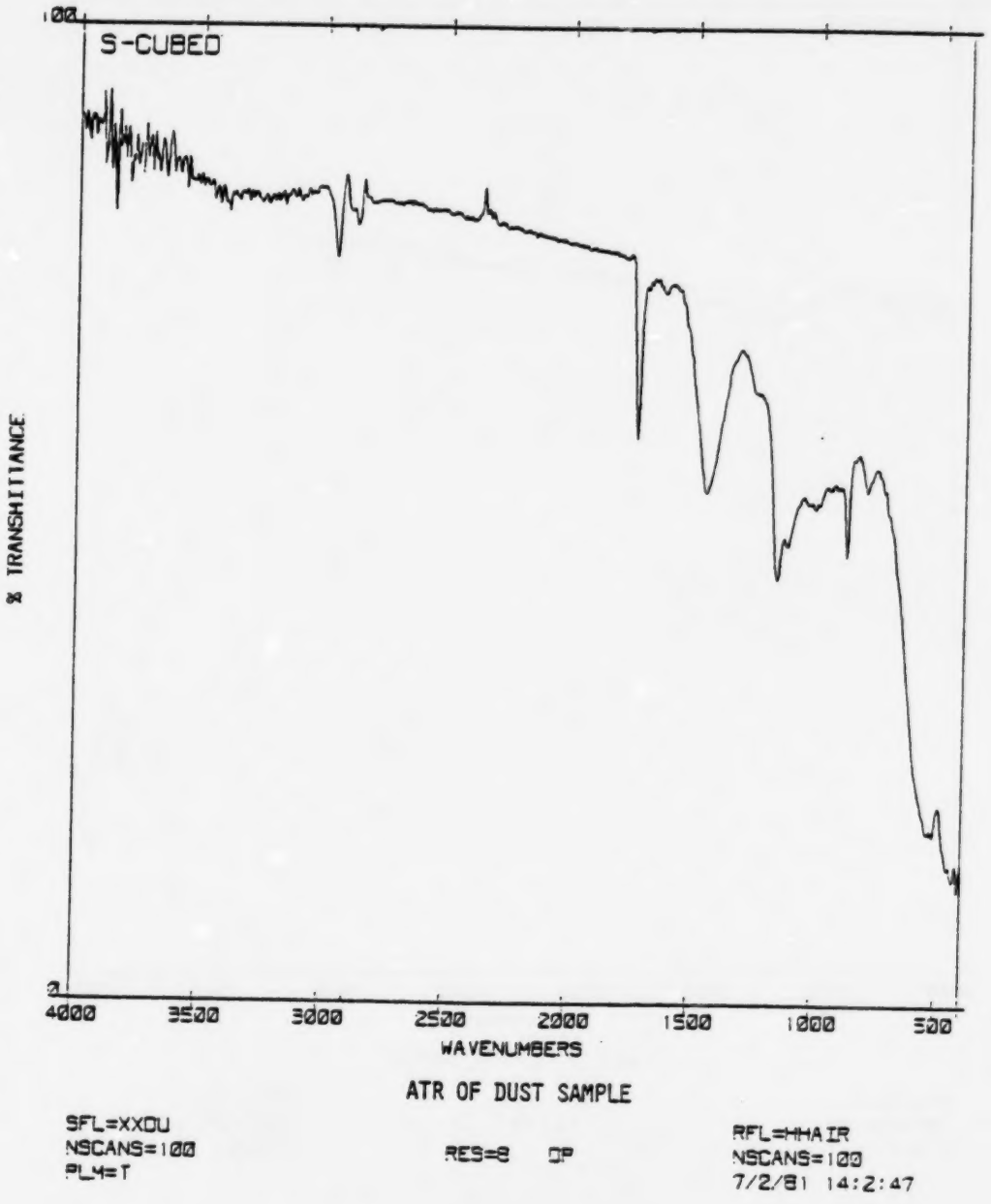


Figure 18. Mid Infrared ATR Spectrum of Steel Mill Emissions

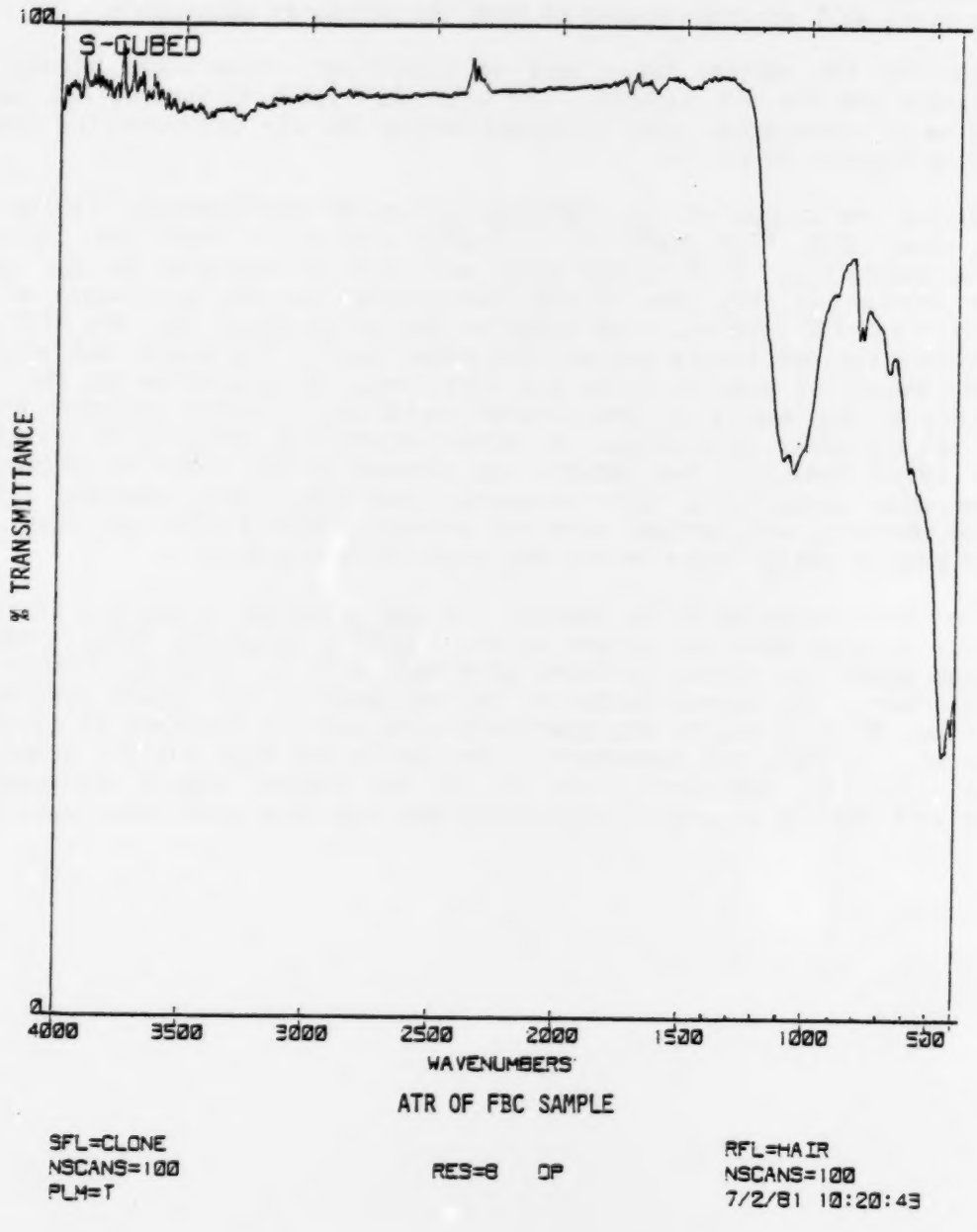


Figure 19. Mid Infrared ATR Spectrum of FBC Emissions

Comparing the spectra in Figures 8 and 18 shows the sample from the steel mill had almost identical transmission and ATR spectra. The only difference was an additional absorbance at 1740 cm^{-1} for the ATR spectrum. The absorbance at 1740 cm^{-1} seemed to be present in all three ATR spectra, but the steel mill spectrum seemed to have the strongest absorbance.

For the FBC sample, there were no significant differences between the transmission and the ATR spectra. The only observable difference was due to missing water absorbances which occurred during the KBr pellet-making process (comparing Figures 10 and 19).

During the course of the characterization of environmental samples, it became clear that FTIR could be a useful analytical tool for inorganic compound speciation. FTIR spectroscopy was able to characterize the copper smelter sample but only gave strong indications for the components of the steel mill and FBC samples. The question had to be asked "why did FTIR work successfully for one sample and not the other two?" The answer was probably that the amount of arsenic oxide was very large in proportion to the other components in the sample or that arsenic oxide was a strong absorber and it masked out the other components. An atomic absorption analysis of the copper smelter sample indicated that arsenic was present on the order of 20 percent, and the other potentially toxic elements (chromium, lead, cadmium, silver, selenium, mercury, and barium) were not present. Analysis of the steel mill and FBC samples proved negative for the above toxic elements.

The sensitivity of IR in general for the detection of various inorganic compounds depends upon the nature of the specific compounds being examined. Compounds which are strong infrared absorbers will be detected easier than weak absorbers. The second factor is the influence of the sample matrix. In some cases, the bulk matrix may completely mask out the presence of any minor components. In fact, one component in the sample may mask out all other components. Finally, the sensitivity of IR for characterizing environmental samples will improve as sample preparation and digestion techniques improve.

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15. Painter, P.C., Y. Yamada, R.G. Jenkins, M.M. Coleman, and P.L. Walker, Jr., "Investigation of Retrogressive Reactions Leading to Carbonization of Solvent-Refined Coal," Fuel, 58, 293 (1979).

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APPENDIX A

INFRARED SPECTRA OF SELECTED INORGANIC COMPOUNDS

Figure	Compound	Figure (a) 4000-400 cm^{-1}	Figure (b) 500-100 cm^{-1}
A1	Hg_2 (I) SO_4	x	x
A2	Hg (II) SO_4	x	x
A3	Hg (I) Cl	x	x
A4	Hg (II) Cl_2	x	x
A5	As_2O_3	x	x
A6	As_2O_5	x	x
A7	$PbSO_4$	x	x
A8	$CaSO_4$ $2H_2O$	x	a
A9	$(NH_4)_2SO_4$	x	x
A10	Na_2SO_4	x	x
A11	$NaVO_3$ (meta)	x	x
A12	Na_3VO_4 (ortho)	x	x
A13	Na_2CrO_4	x	x
A14	$Na_2Cr_2O_7$	x	x
A15	$NaNO_3$	x	x
A16	NH_4NO_3	x	x
A17	Na_2SO_3	x	x
A18	$NaNO_2$	x	x
A19	Na_2SeO_3	x	x

[a] $CaSO_4$ (dried and heated)

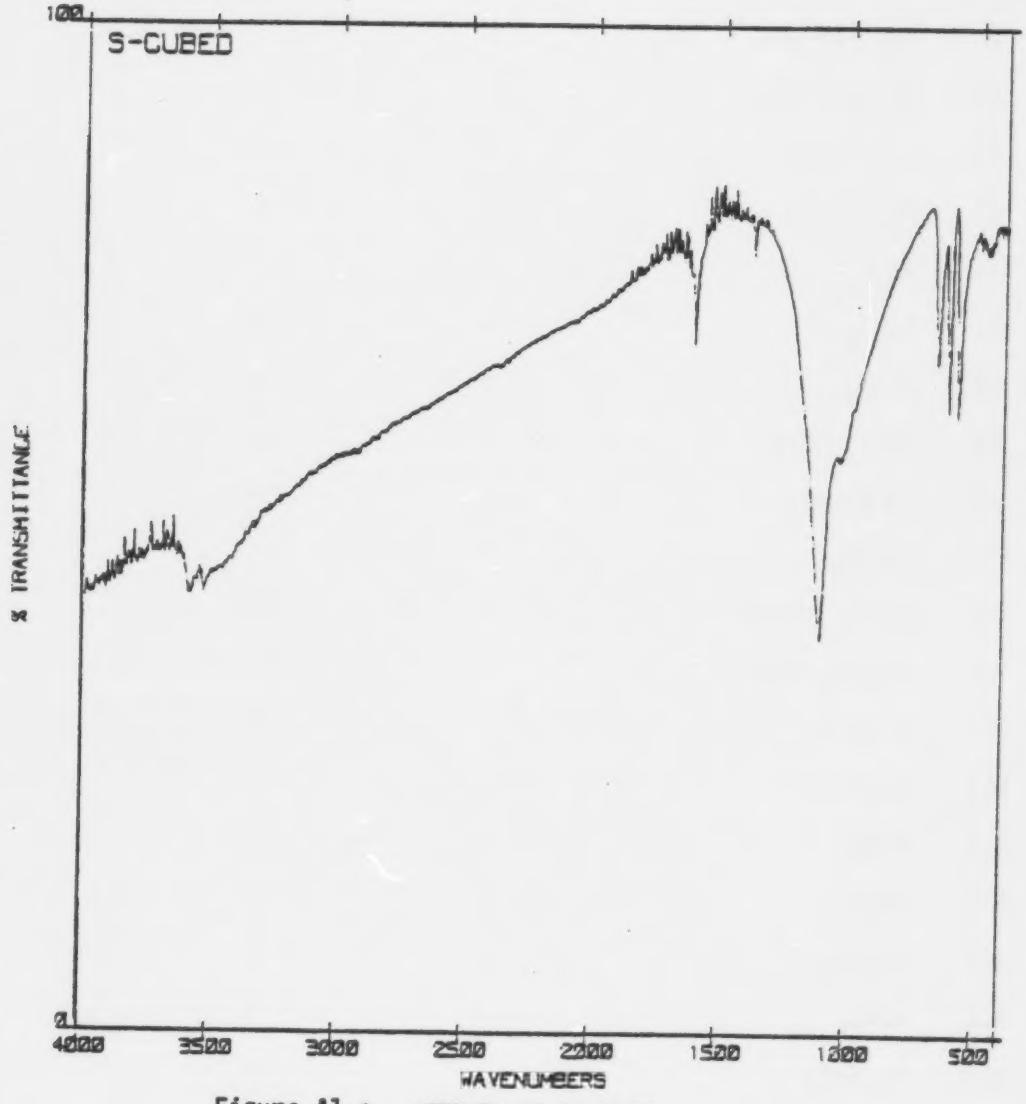

Figure A1-a. MERCURY(I) SULFATE

SFL=HSGH
NSCANS=100
FLM=T

RES=4 DP

RFL=EA IR
NSCANS=100
4/2/81 9:38:25

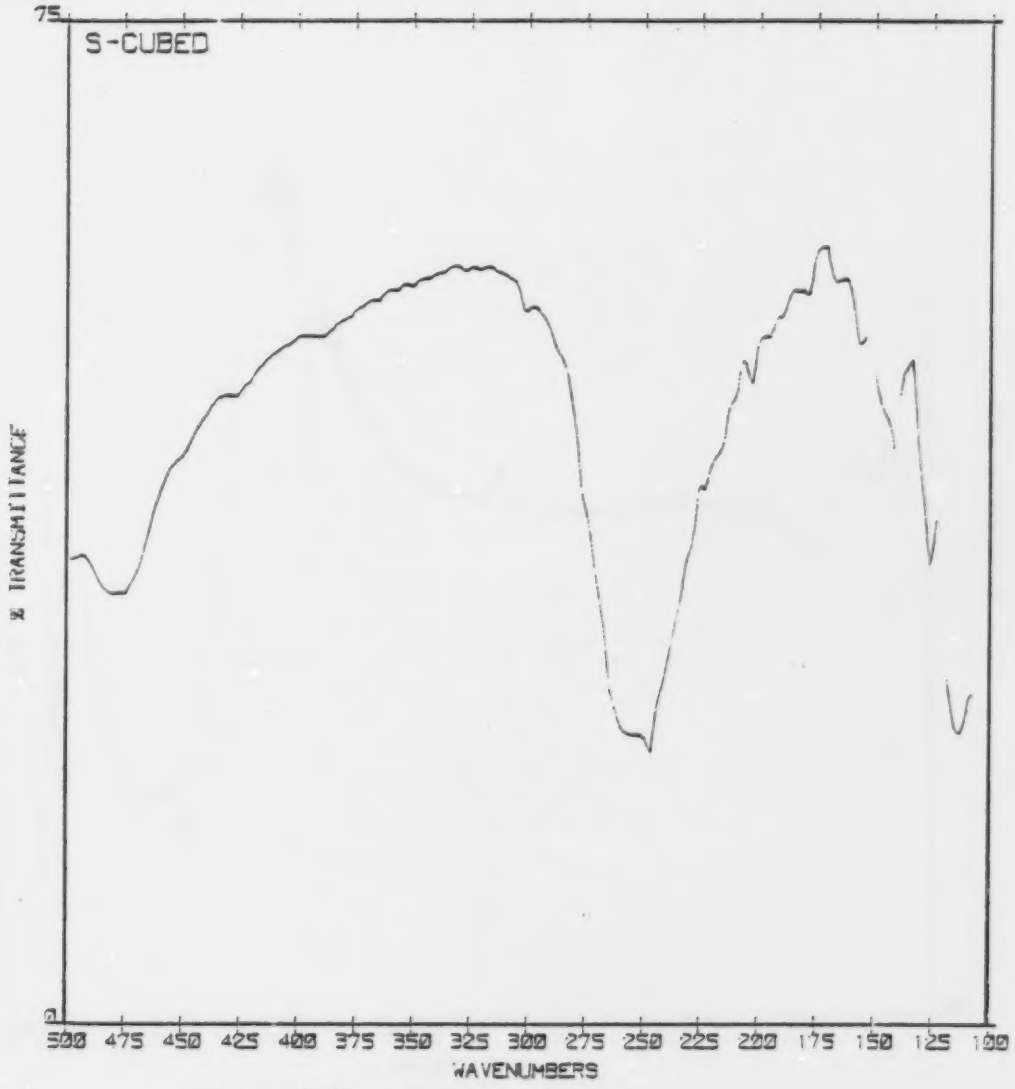

Figure A1-b. MERCURY (I) SULFATE

SFL=FHSLO
NSCANS=100
PLM=T

RES=4 CP

RFL=CAIR
NSCANS=100
4/16/91 10:05:5

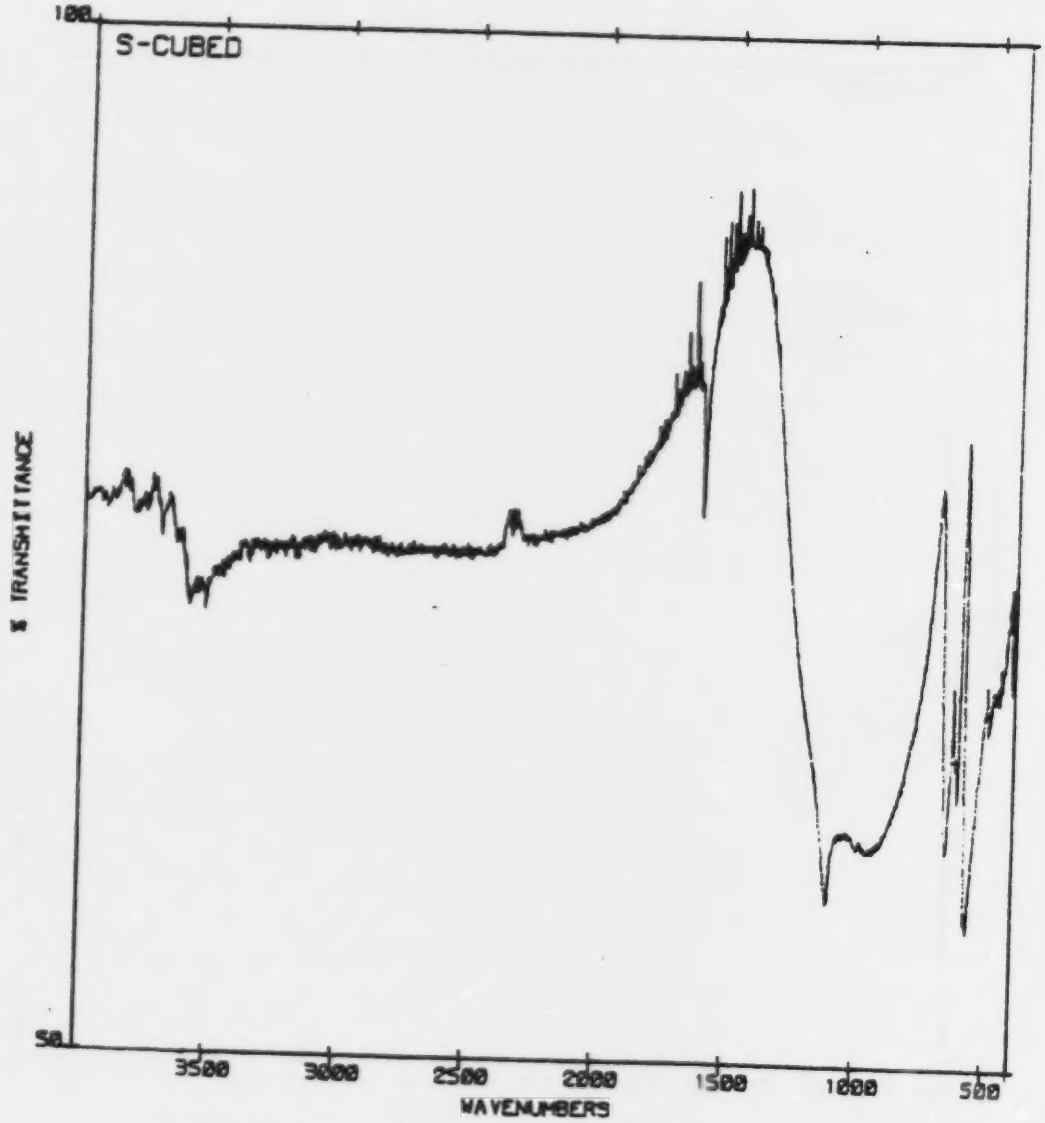

Figure A2-a. MERCURY (II) SULFATE

SFL=HG3O4REP
NSCANS=400
PLM=T

RES=4 DP

RFL=REF0229A
NSCANS=400
2/29/84 13:4:6

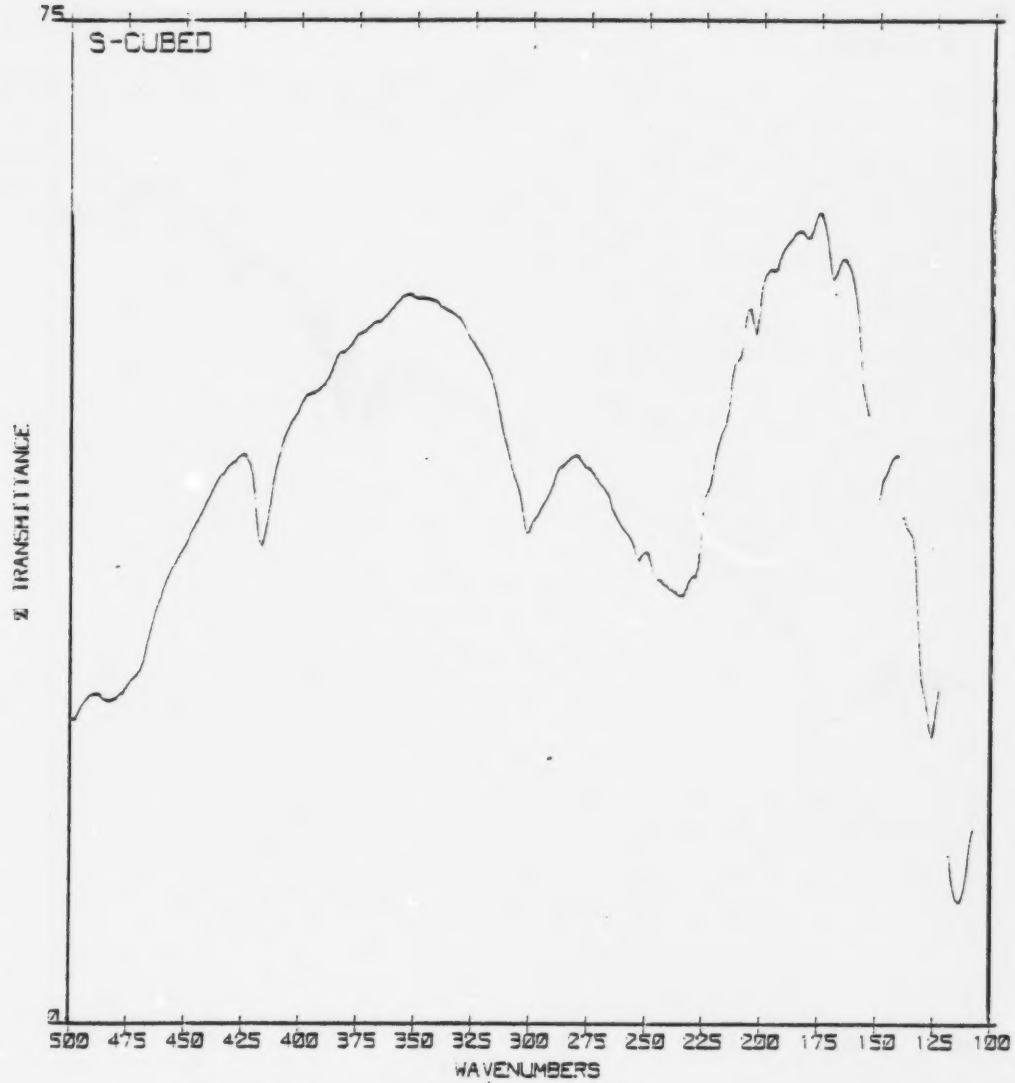

Figure A2-b. MERCURY (II) SULFATE

SFL=FHSOL
NSCANS=100
PLM=T

RES=4 CP

RFL=CAIR
NSCANS=100
4/16/91 10:12:.6

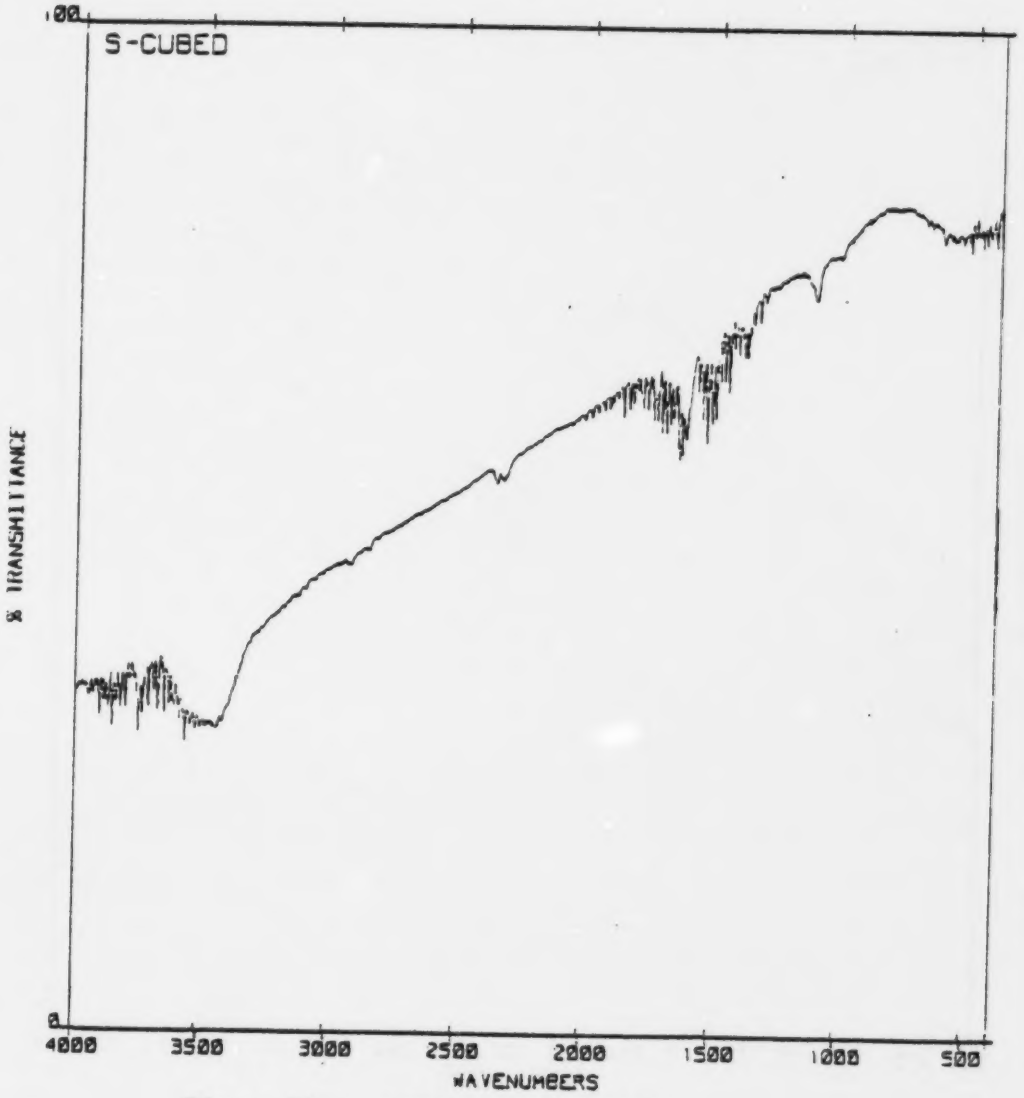

Figure A3-a. MERCURY (I) CHLORIDE

SFL=MERCH
NSCANS=100
PLM=T

RES=4 DP

RFL=MAIR
NSCANS=100
3/24/91 16:21:36

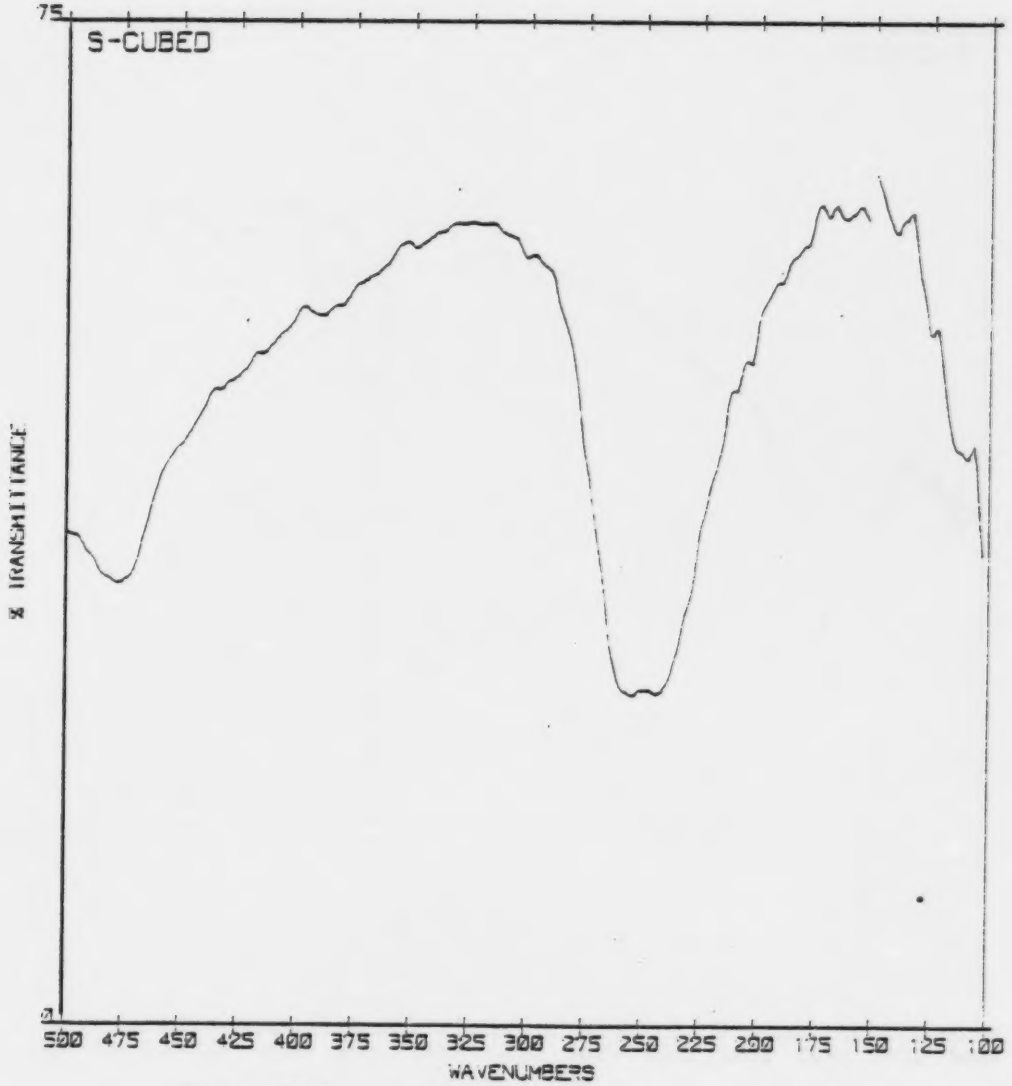

Figure A3-b. MERCURY (I) CHLORIDE

SFL=FMEDL
NSCANS=100
PL4=T

RES=4 DP

RFL=TAIR
NSCANS=100
4/15/81 11:38:45

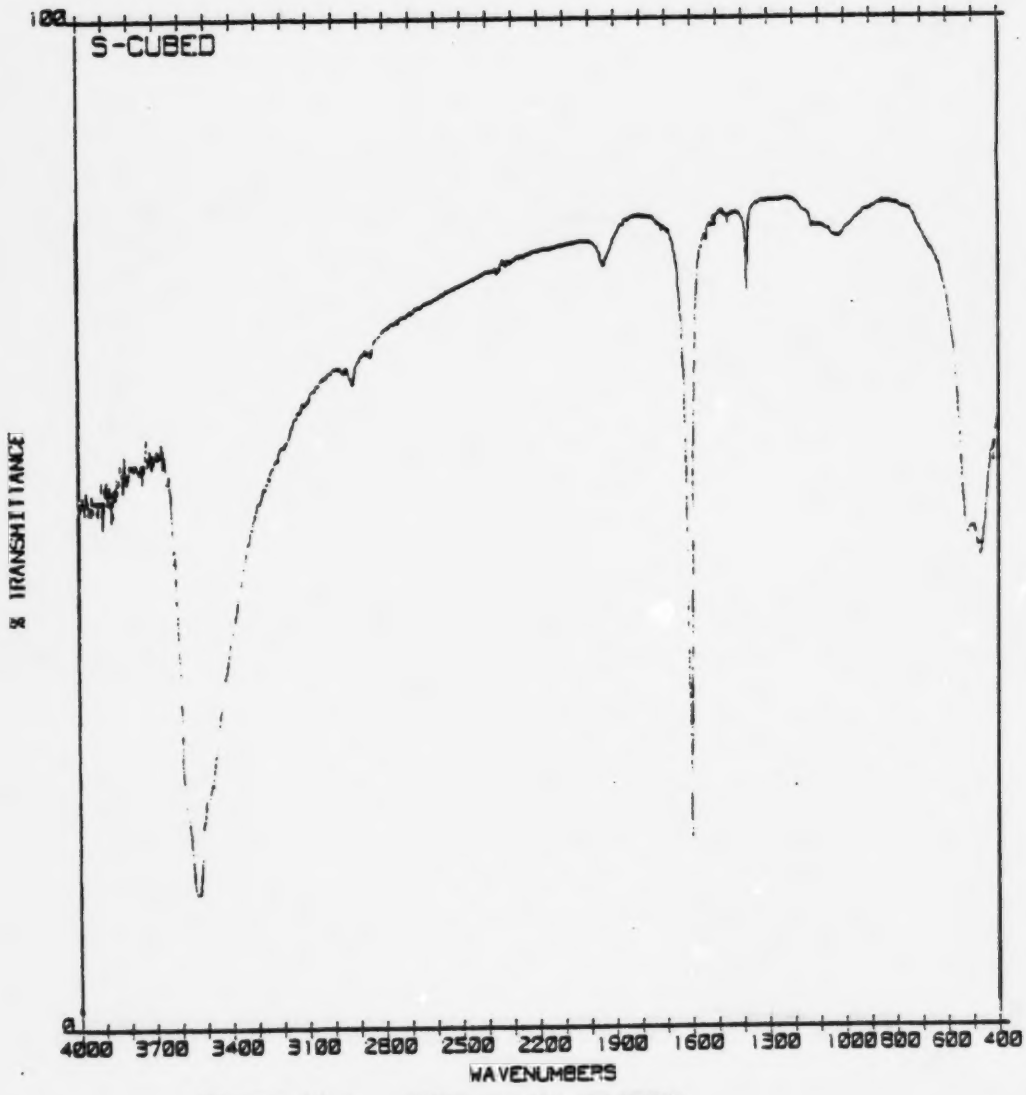

Figure A4-a. MERCURY (II) CHLORIDE

SFL=0L0
NSCANS=100
PLM=T

RES=4 OP

RFL=000
NSCANS=100
5/15/81 14:50:52

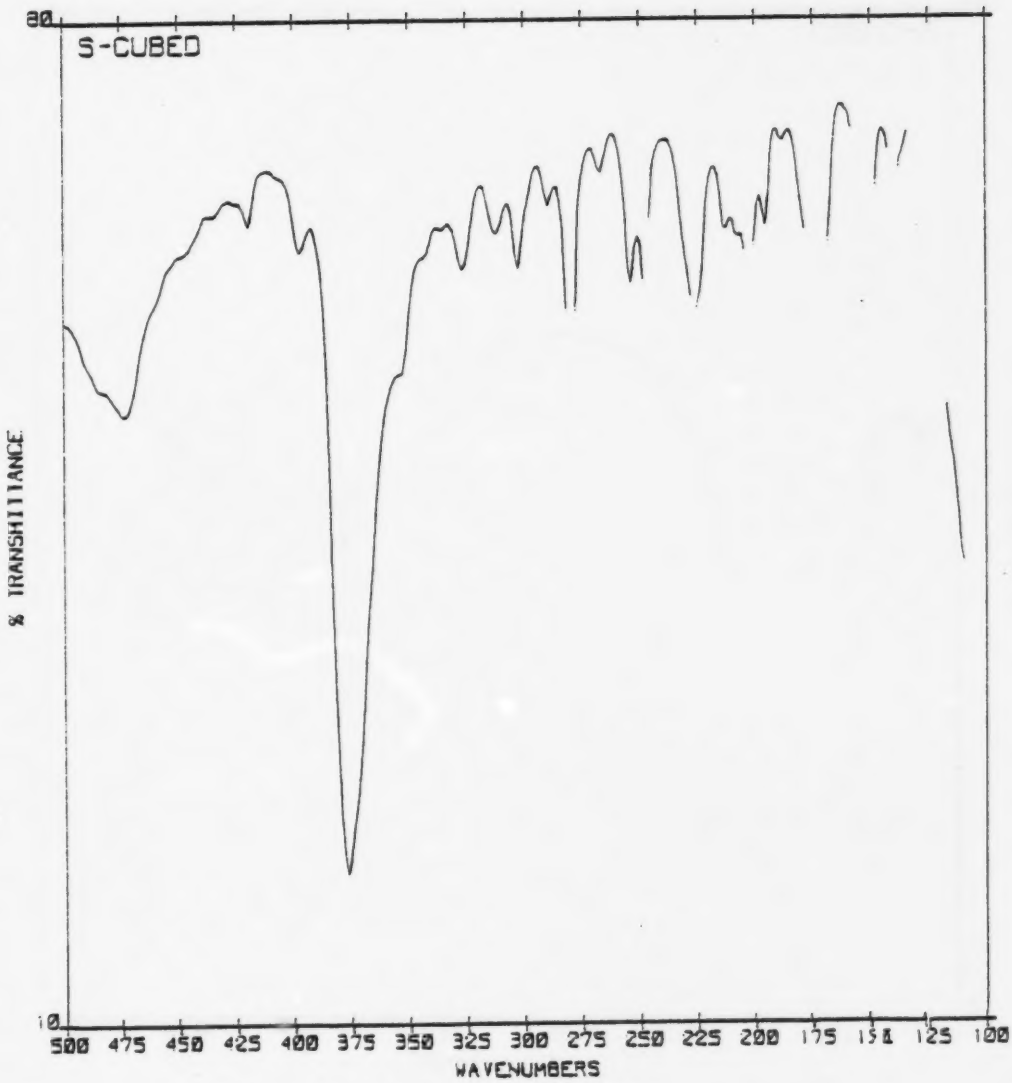

Figure A4-b. MERCURIC CHLORIDE

SFL=EMM
NSCANS=100
PLM=T

RES=4 OP

RFL=JKA
NSCANS=100
5/12/81 14:42:20

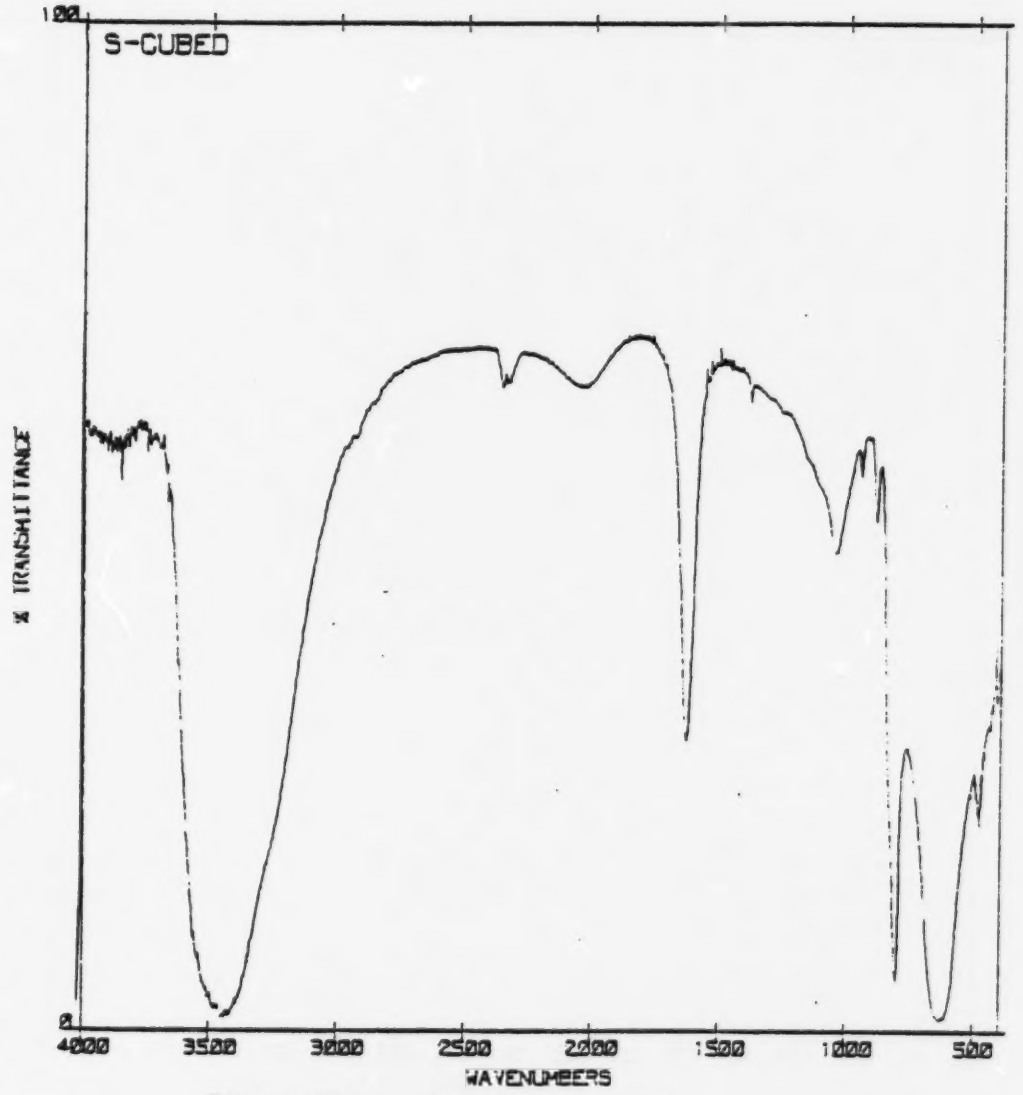

Figure A5-a. ARSENIC(III) OXIDE

SFL=AROX
NSCANS=100
PL=T

RES=4 CP

SFL=MAIR
NSCANS=100
4/1/31 14:52:13

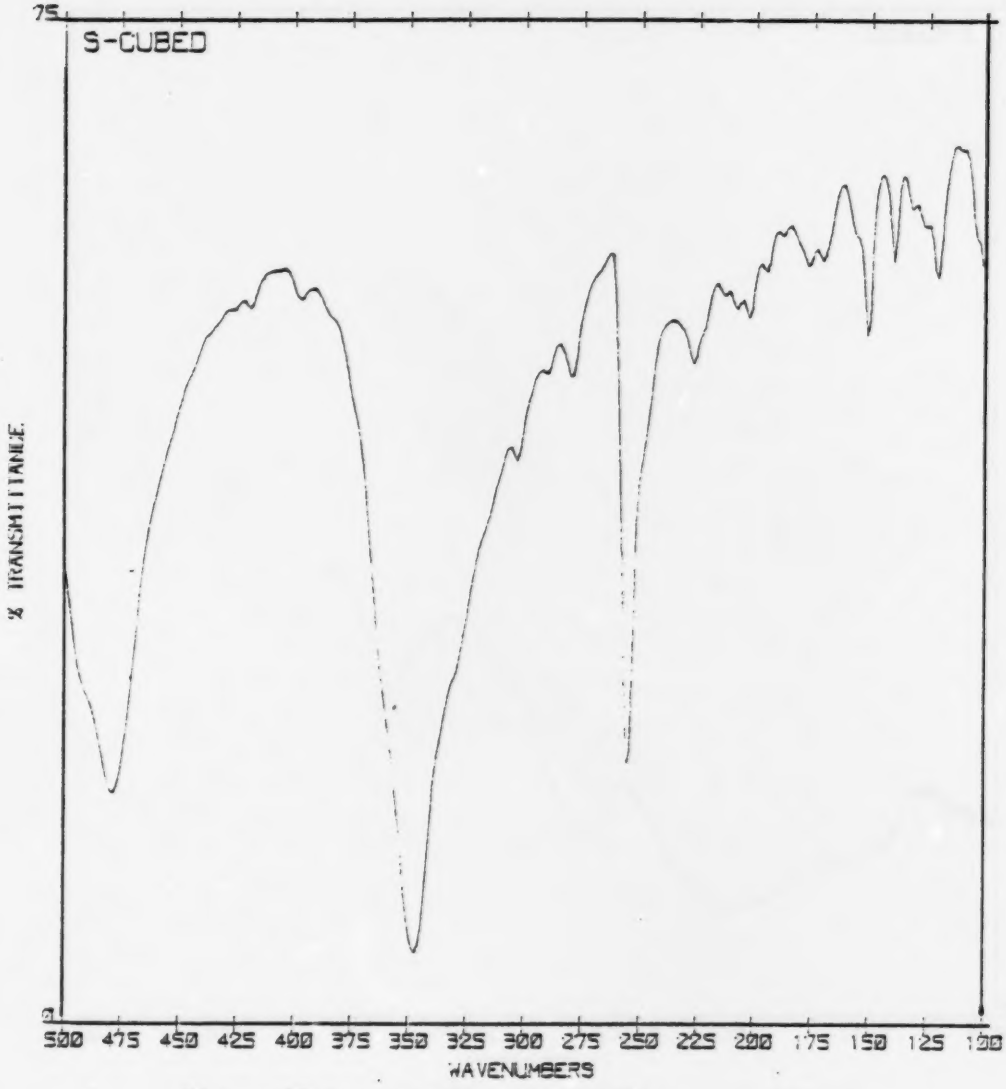

Figure A5-b. ARSENIC (III) OXIDE

SFL=FAS3
NSCANS=100
FLM=T

RES=4 JP

RFL=ITAIR
NSCANS=100
4/15/81 11:41:23

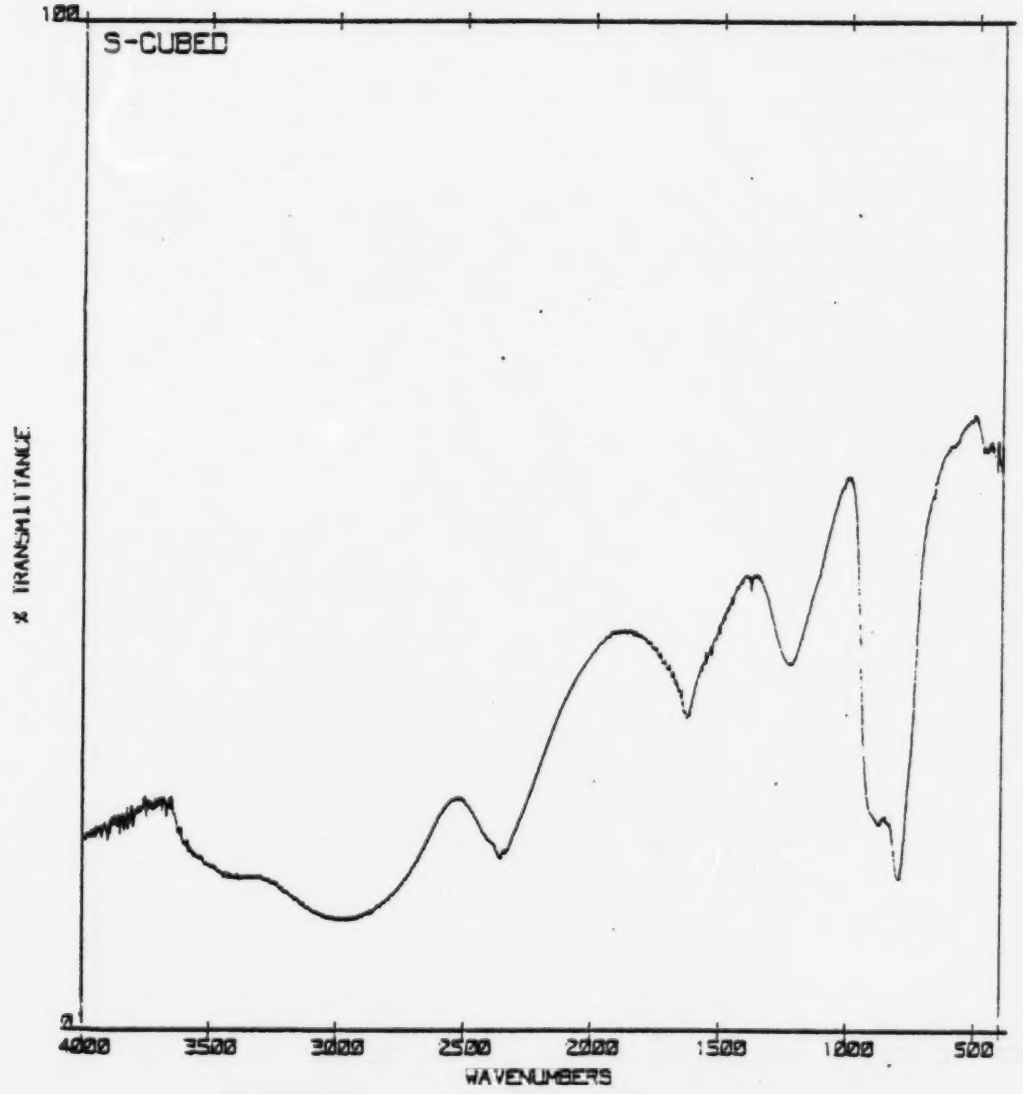

Figure A6-a. ARSENIC(V) OXIDE

SFL=ARRO
NSCANS=100
PLM=T

RES=4 DP

RFL=MAIP
NSCANS=100
4/1/81 14:58:56

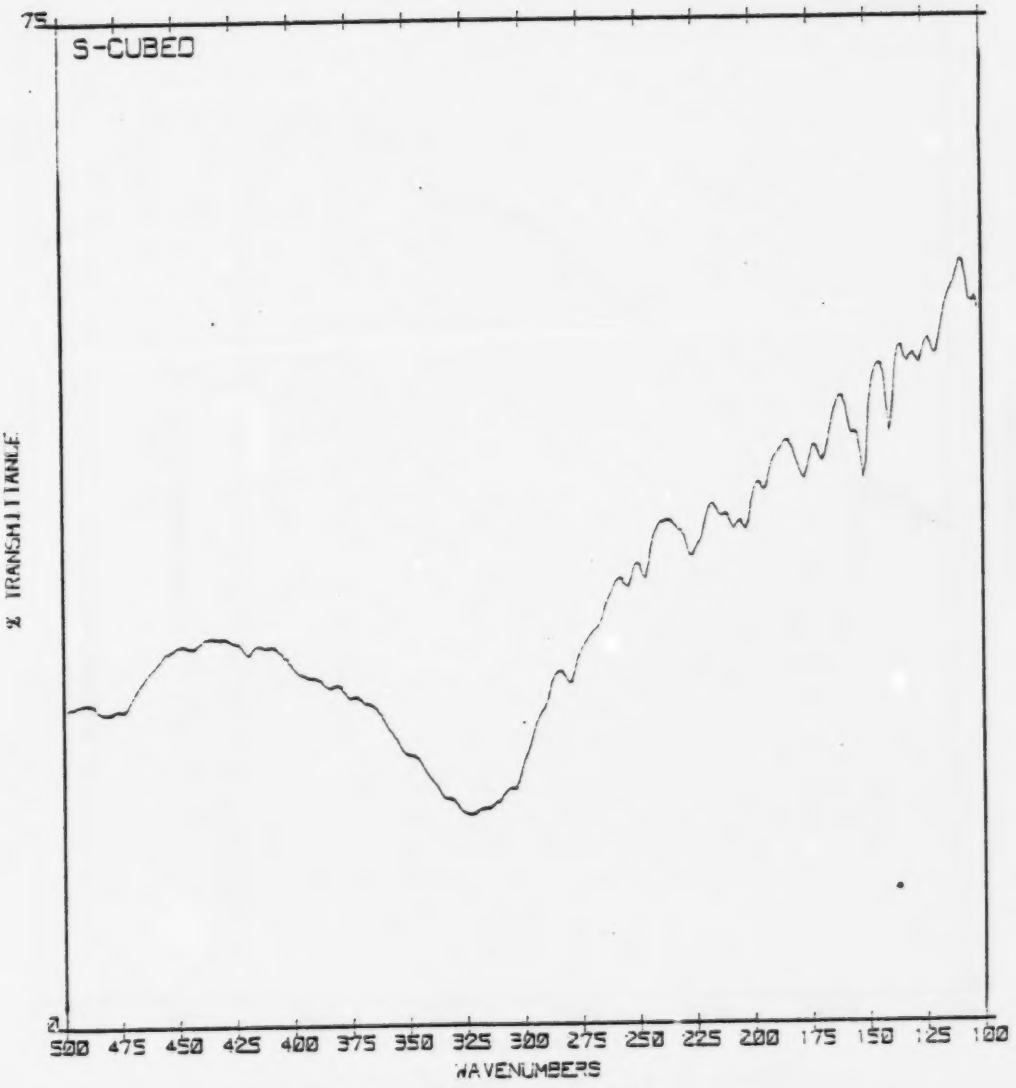

Figure A6-b. ARSENIC (V) OXIDE

SFL=FASS
NSCANS=100
PLM=T

RES=4 CP

RFL=TTAIR
NSCANS=100
4/15/81 11:37:29

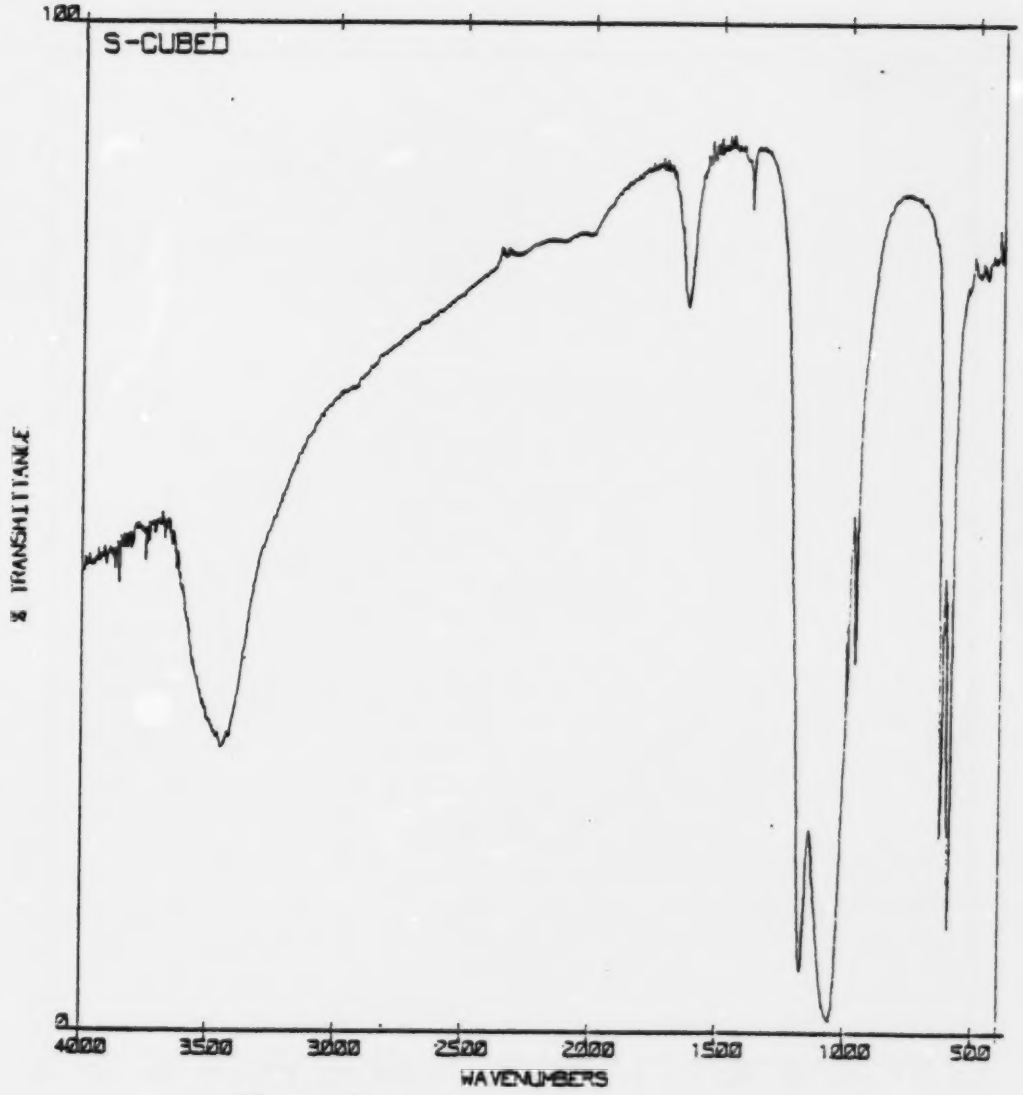

Figure A7-a. LEAD SULFATE

SFL=LESU
NSCANS=100
PLM=1

RES=4 DP

RFL=MAIR
NSCANS=100
3/24/81 16:40:38

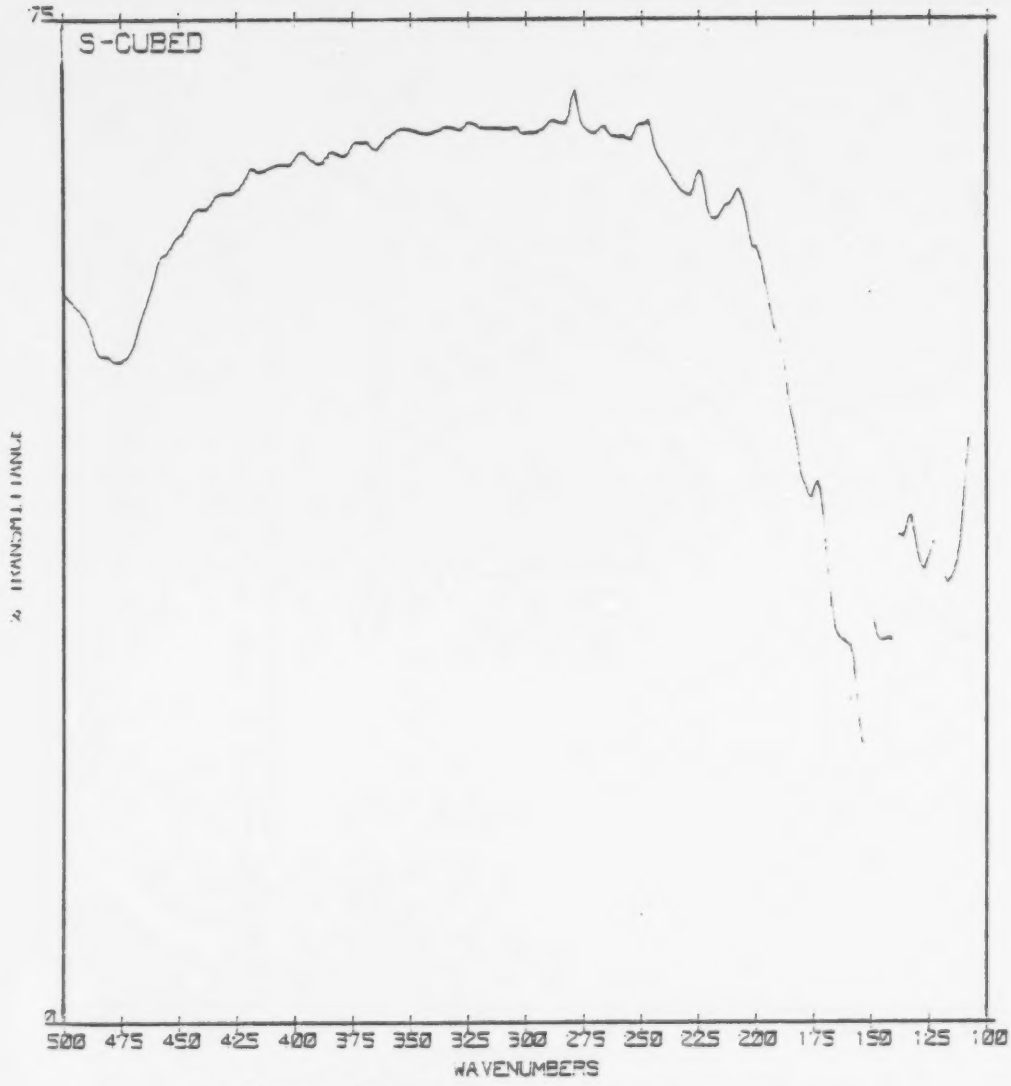

Figure A7-b. LEAD SULFATE

SFL=FPBS
NSCANS=100
PL4=T

RES=4 DP

RFL=CAIR
NSCANS=100
4/16/91 10:14:16

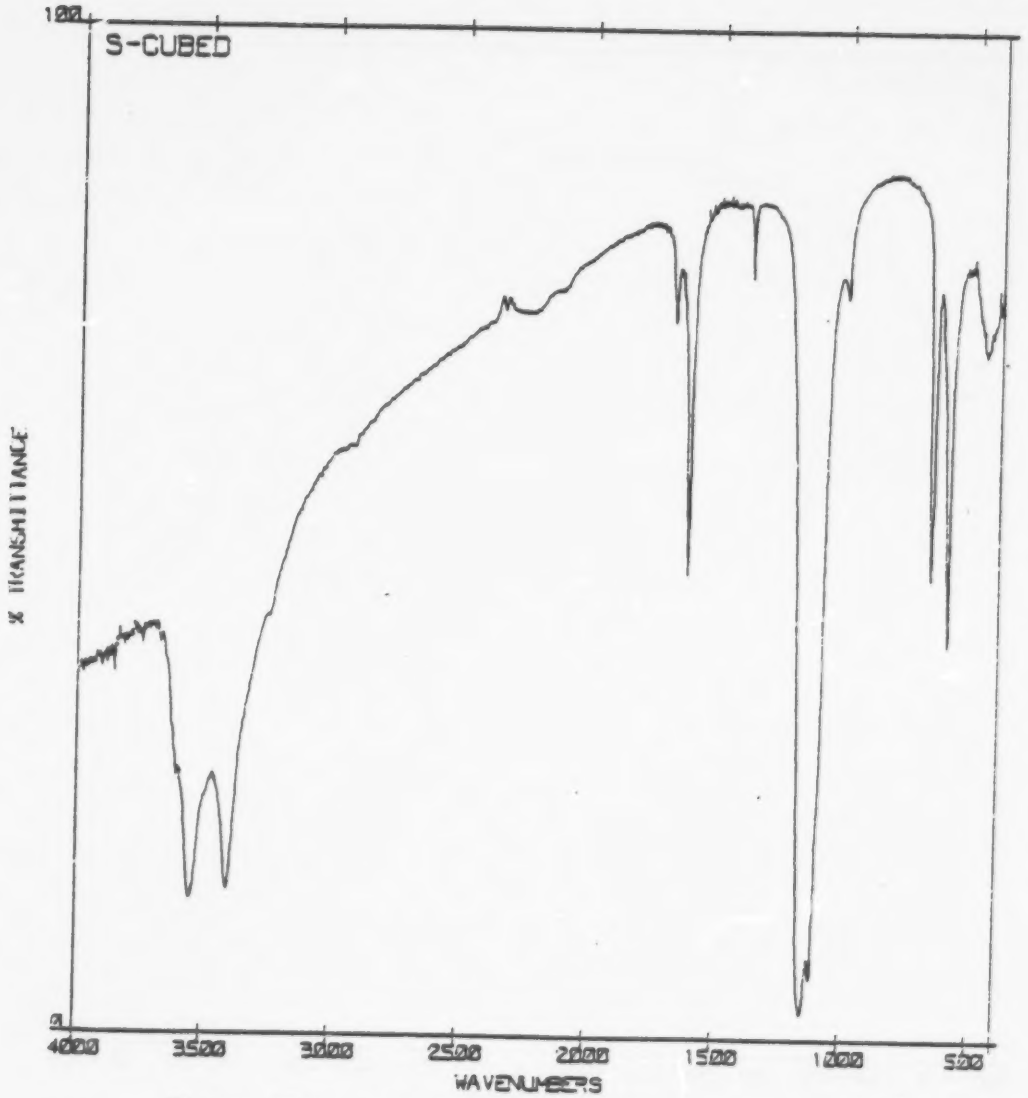

Figure A8-a. CALCIUM SULFATE DIHYDRATE

SFL=CASU
NSCANS=100
PLM=T

RES=4 DP

RFL=MAIR
NSCANS=100
3/24/81 16:52:45

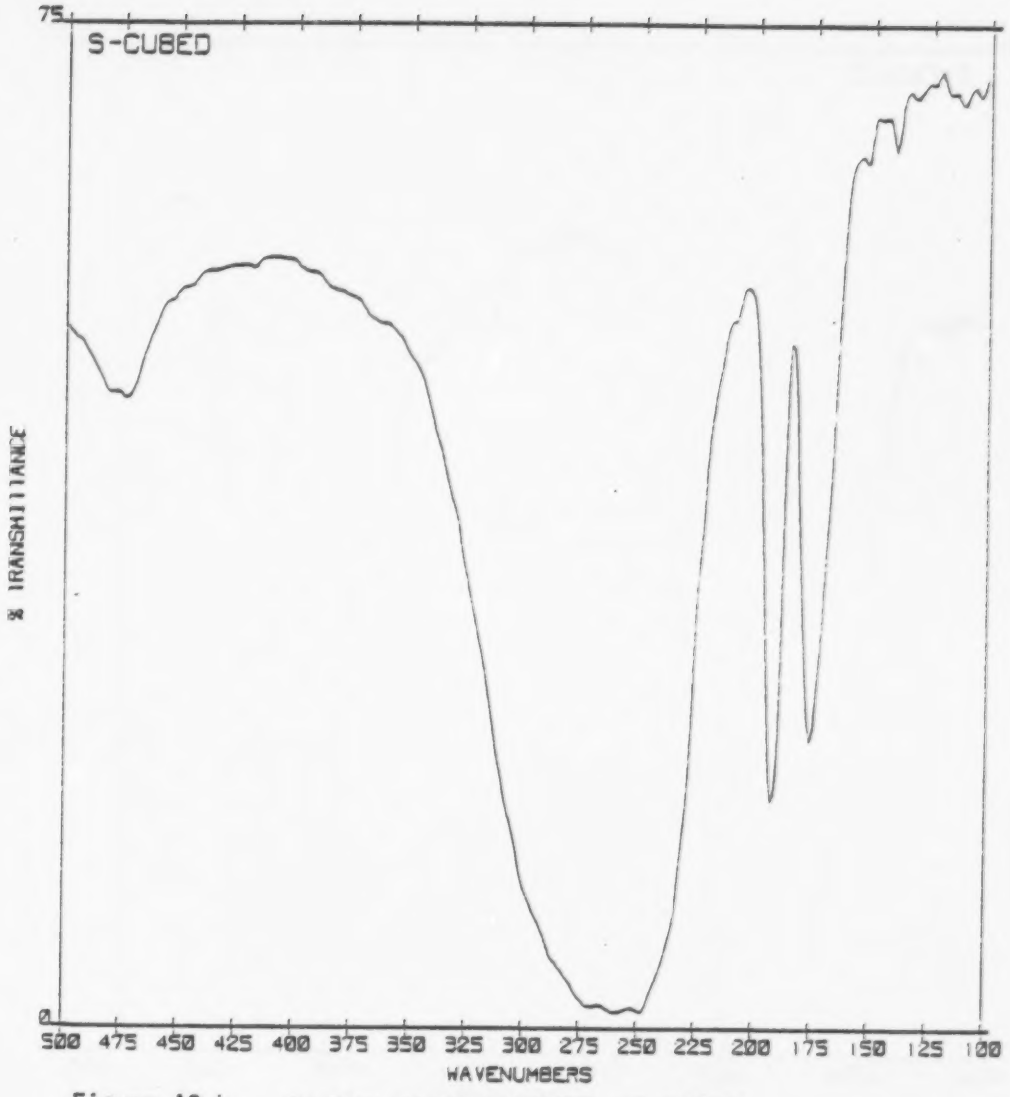

Figure A8-b. CALCIUM SULFATE (HEATED AND PURGED)

SFL=CHOT
NSCANS=100
PLM=T

RES=4 DP

RFL=QWQ
NSCANS=100
4/20/81 12:55:59

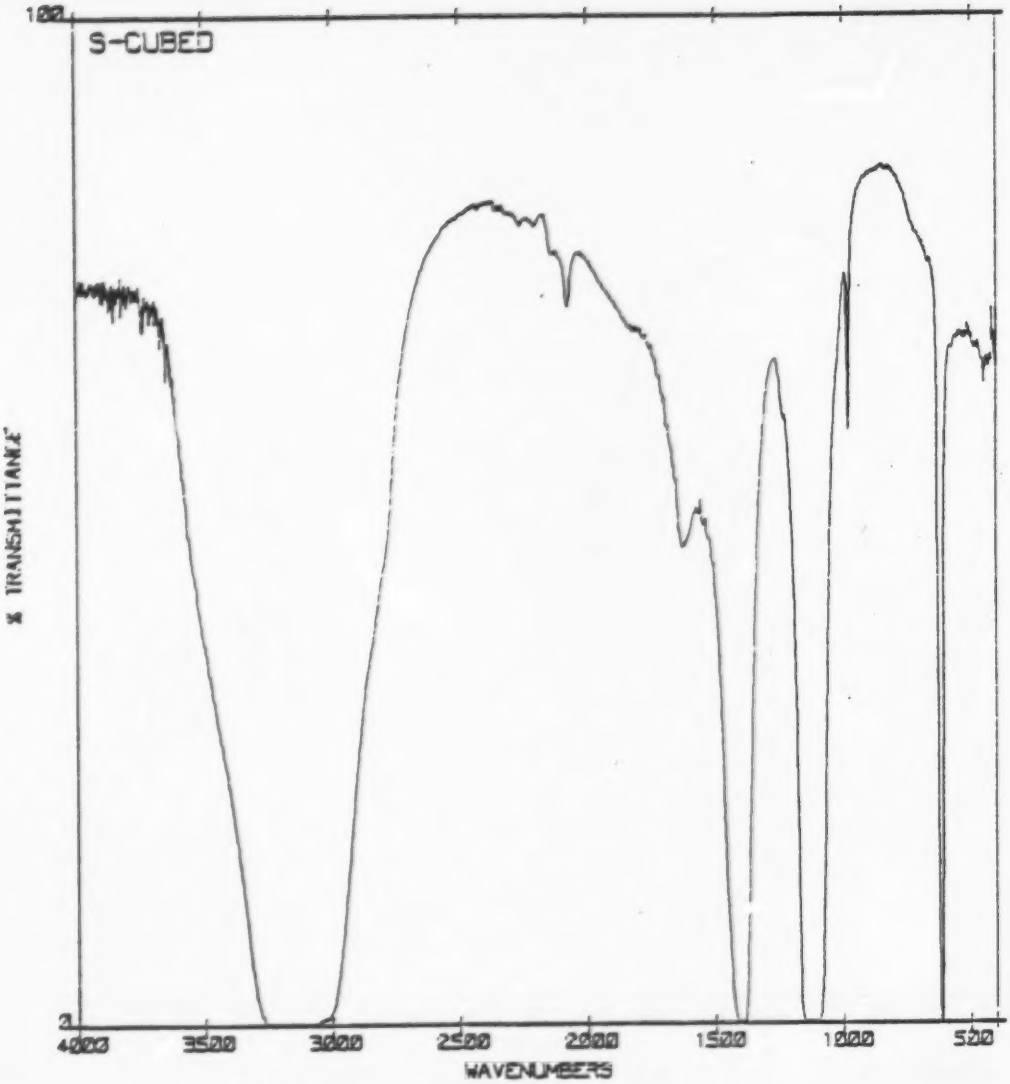

Figure A9-a. AMMONIUM SULFATE

SFL=NH4SU
NSCANS=100
PL4=T

RES=4 DP

RFL=MAIR
NSCANS=100
3/24/81 15:56:26

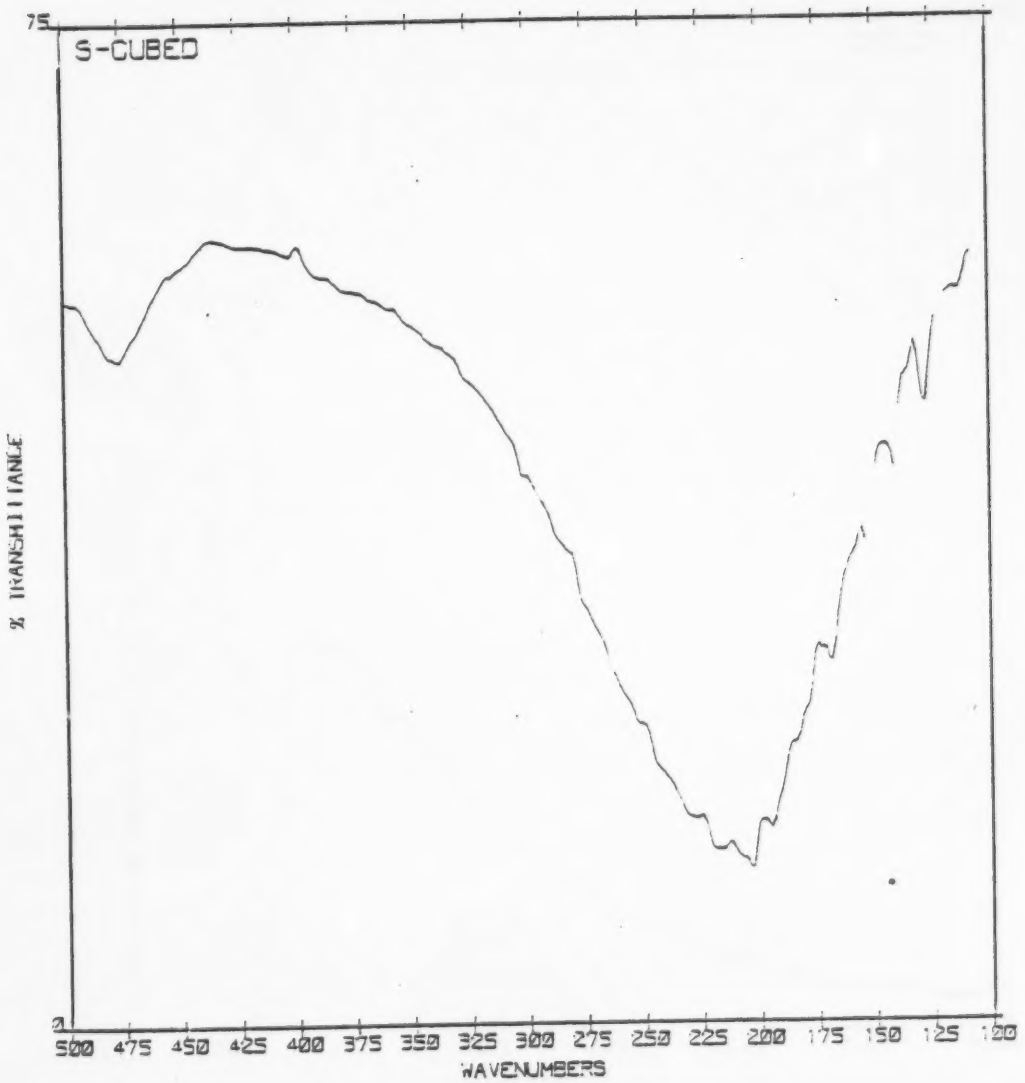

Figure A9-b. AMMONIUM SULFATE

SFL=FNHSO
NSCANS=100
PLM=T

RES=4 OP

RFL=CAIR
NSCANS=100
4/16/91 10:15:56

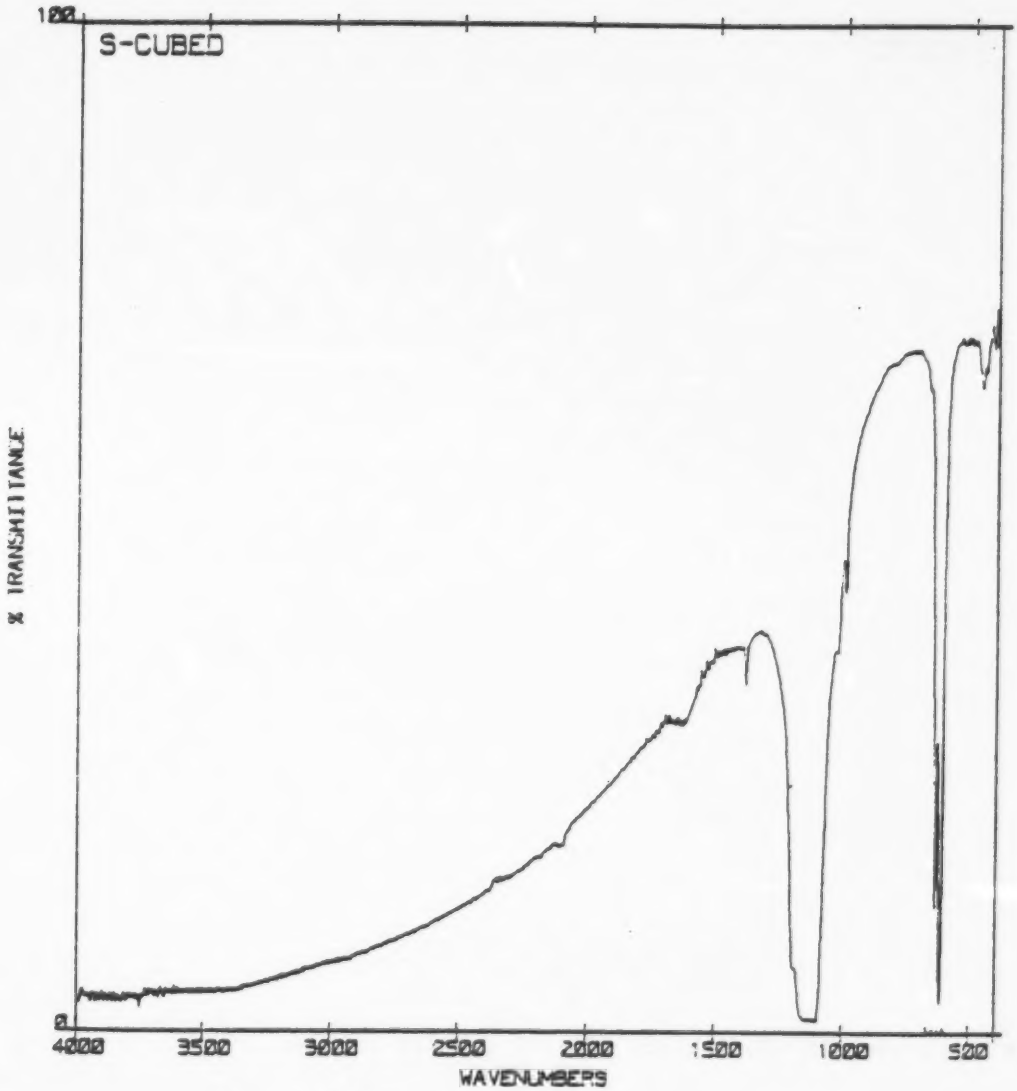

Figure A10-a. SODIUM SULFATE

SFL=AZZ
NSCANS=100
PLM=T

RES=4 DP

RFL=XAIR
NSCANS=100
2/12/81 10:55:39

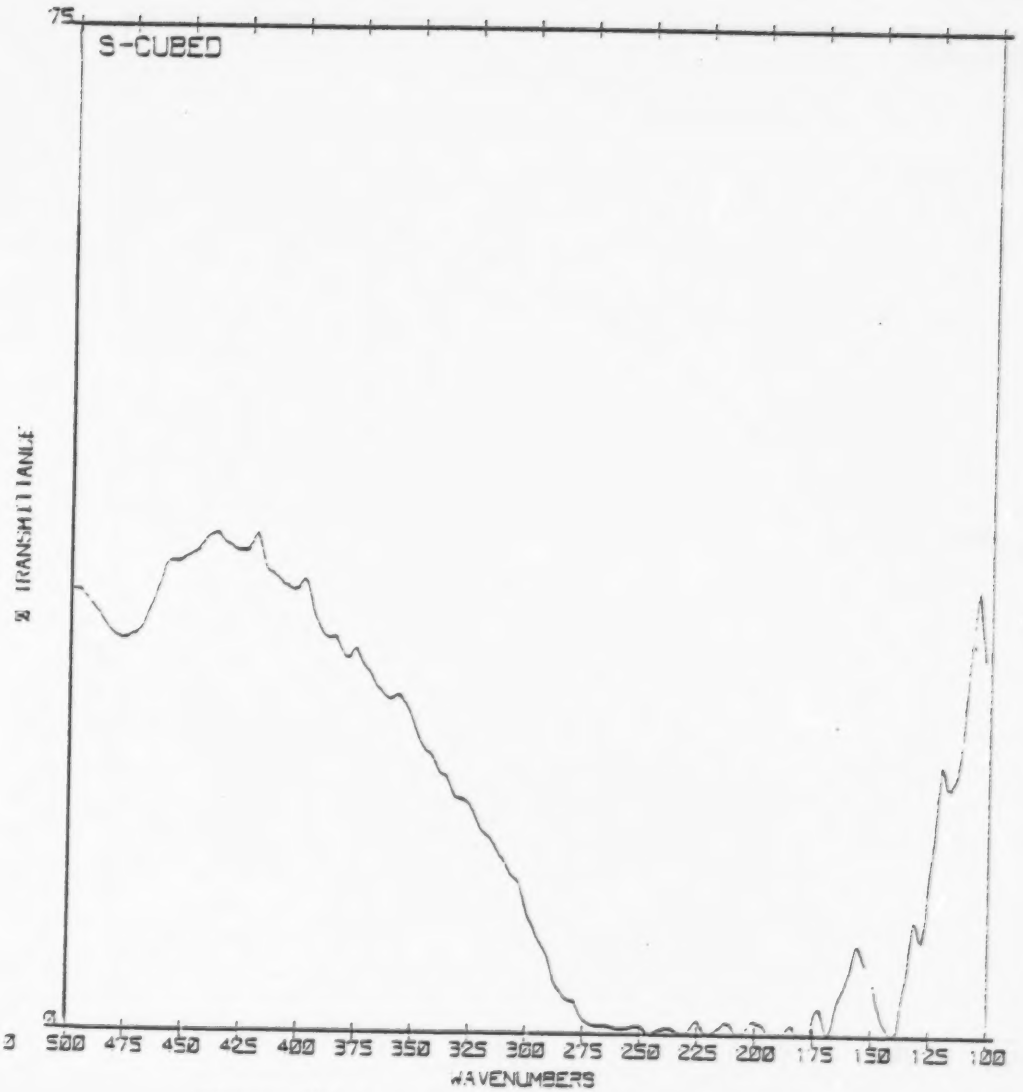

Figure A10-b. SODIUM SULFATE

SFL=FNSO4
NSCANS=100
RES=4 DP
RFL=TAIR
NSCANS=100
4/15/81 11:46:35

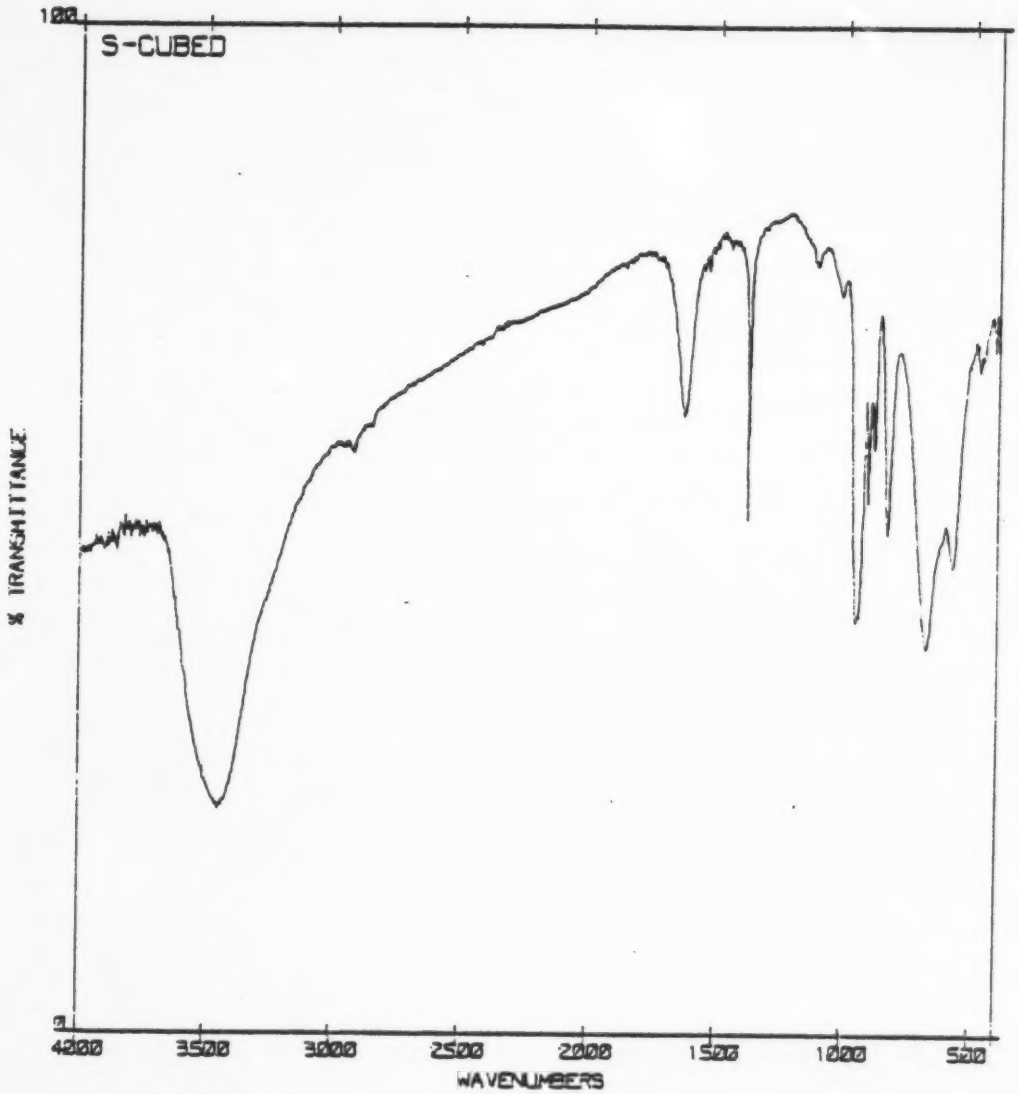

Figure A11-a. SODIUM VANADATE META

SFL=META
NSCANS=100
FL=T

RES=4 DP

RFL=TAIR
NSCANS=100
3/25/91 10:57:32

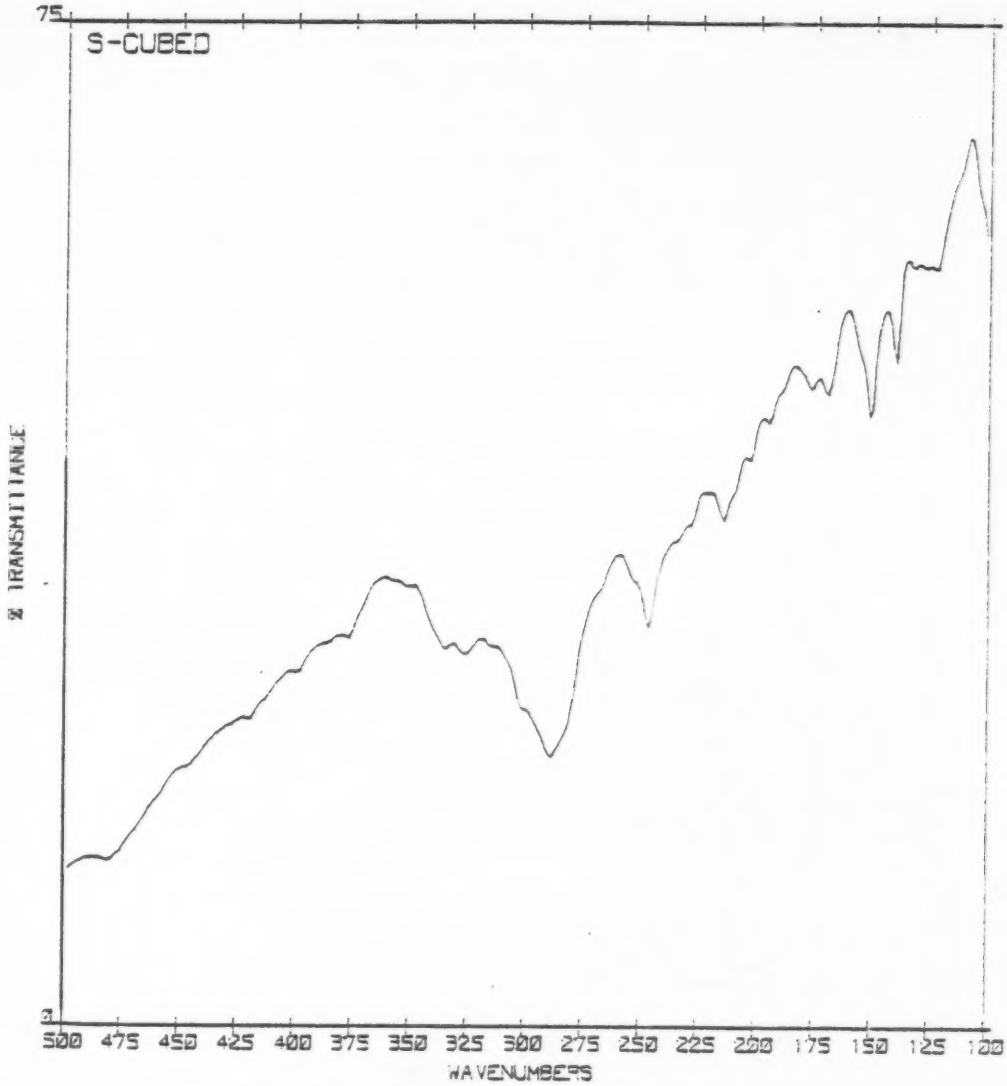

Figure A11-b. SODIUM VANADATE META

SFL=FNVOM
NSCANS=100
PLM=T

RES=4 DP

RFL=TTAIP
NSCANS=100
4/15/81 11:31:5

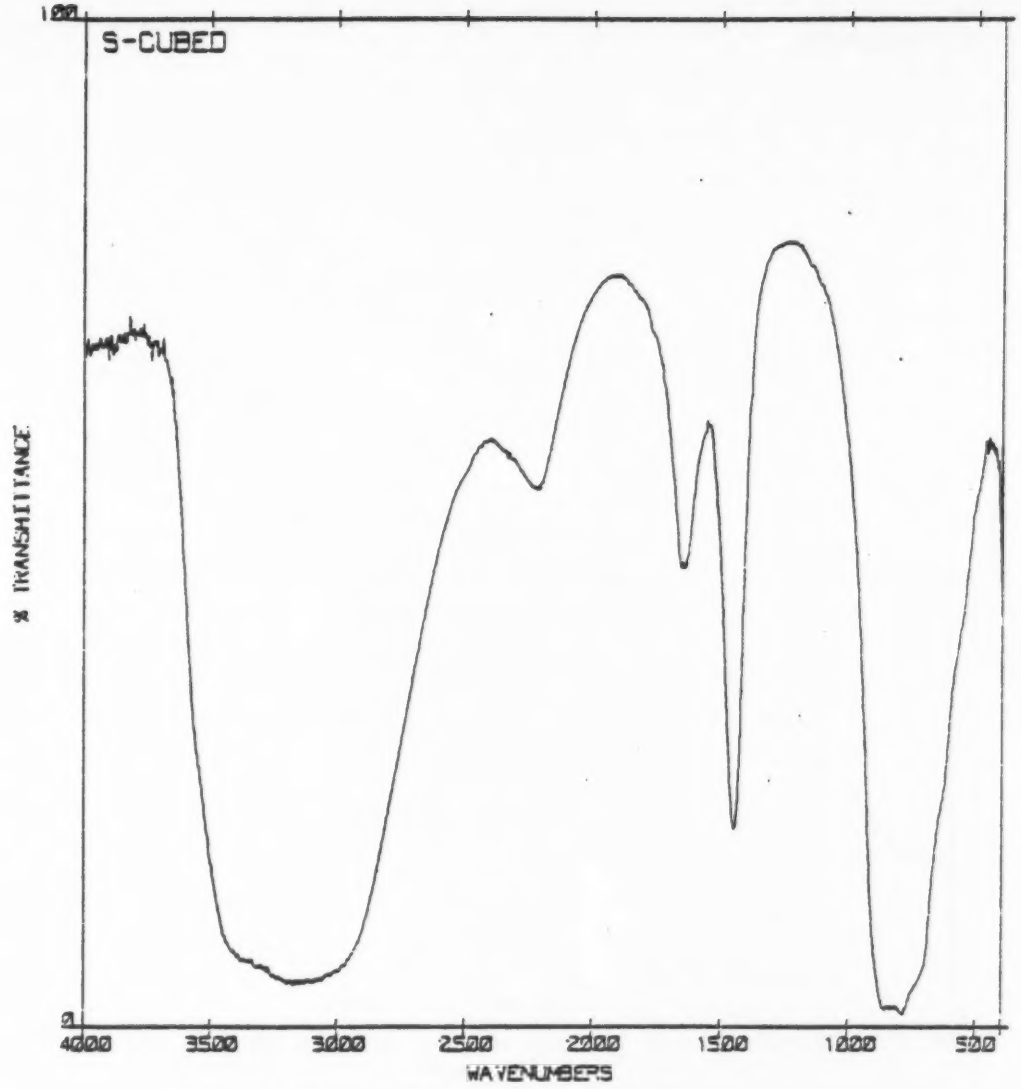

Figure A12-a. SODIUM VANADATE ORTHO

SFL=SOVA
NSCANS=100
PLW=T

RES=4 DP

RFL=MAIR
NSCANS=100
3/24/81 16:28:36

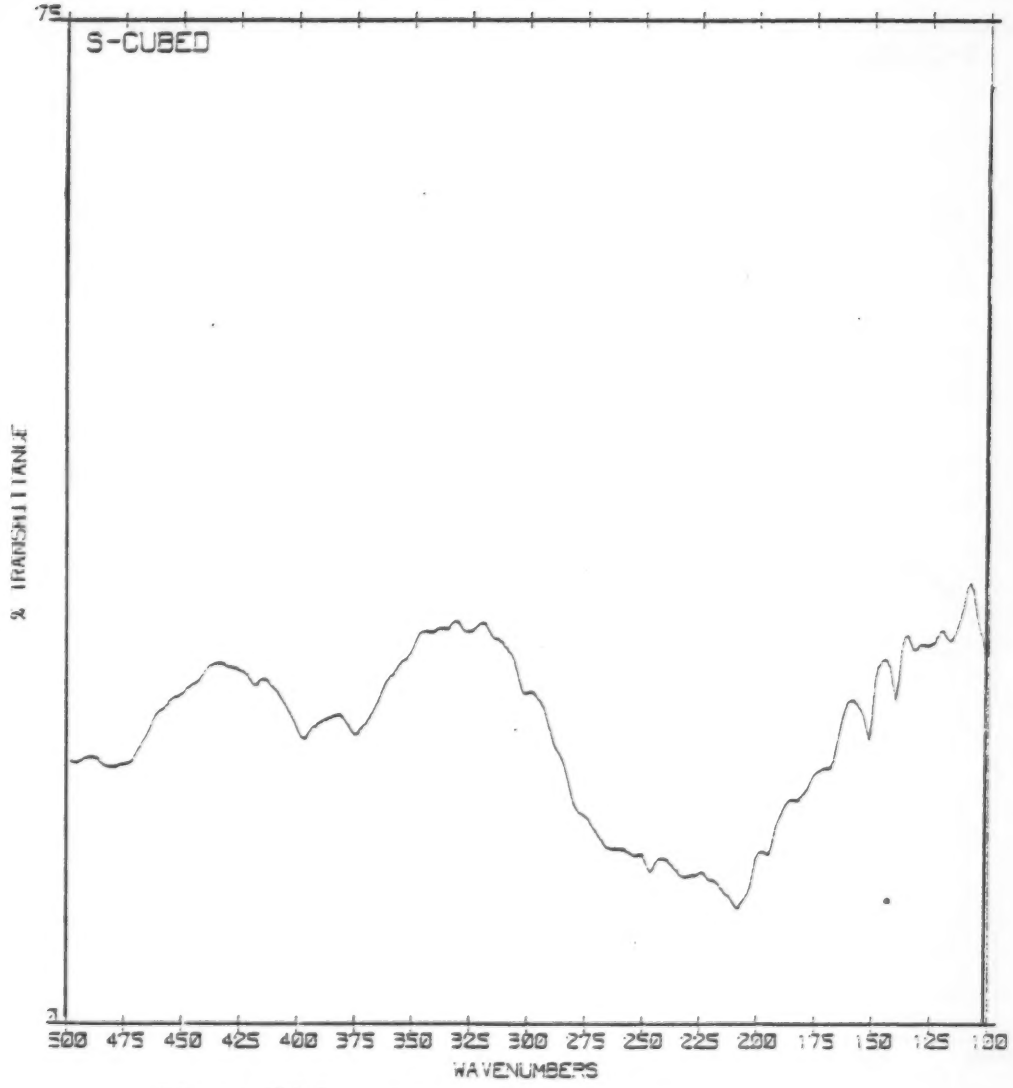

Figure A12-b. SODIUM VANADATE ORTHO

SFL=FNVCO
NSCANS=100
PL_M=T

RES=4 CP

RFL=TTAIR
NSCANS=100
4/15/81 11:29:2

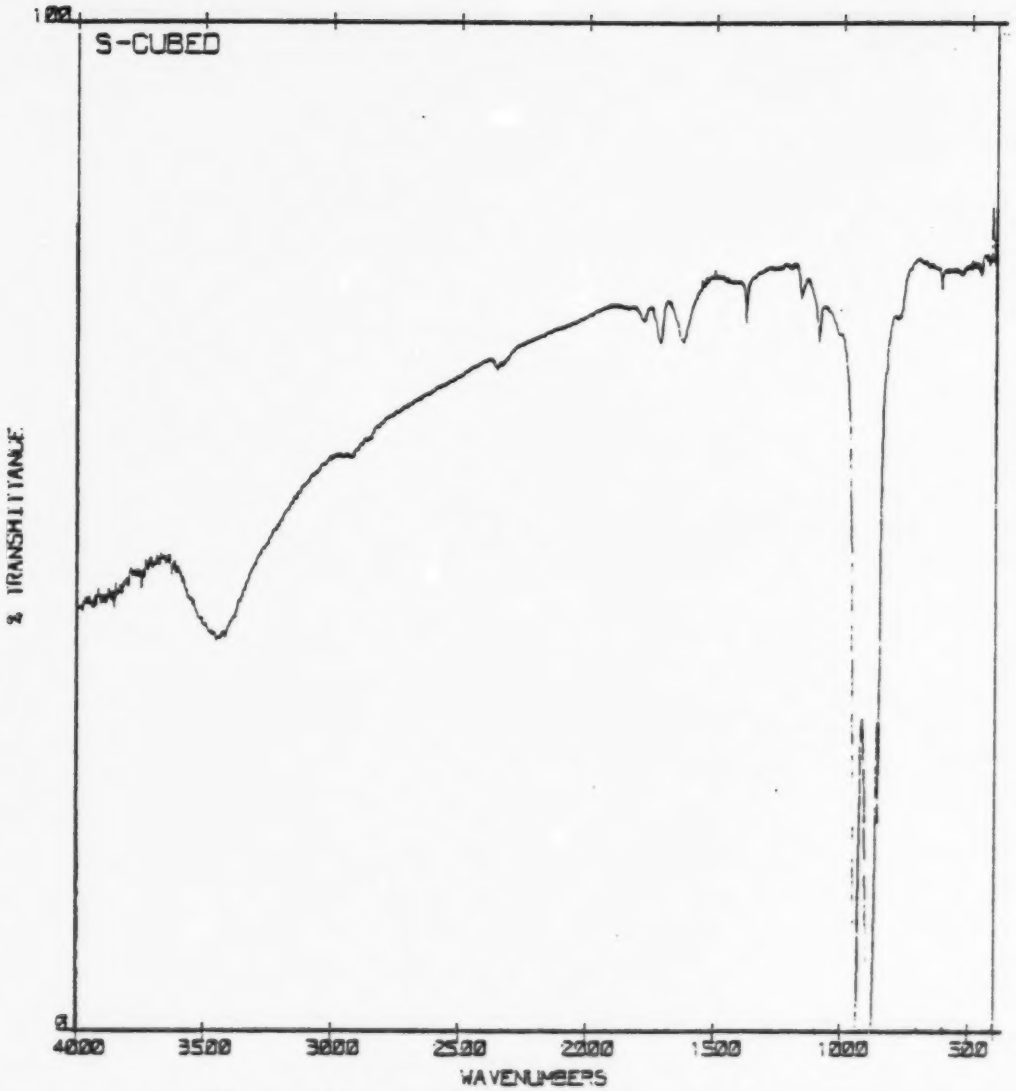

Figure A13-a. SODIUM CHROMATE

SFL=NACR
NSCANS=100
PLM=T

RES=4 DP

RFL=MAIR
NSCANS=100
4/1/91 15:55

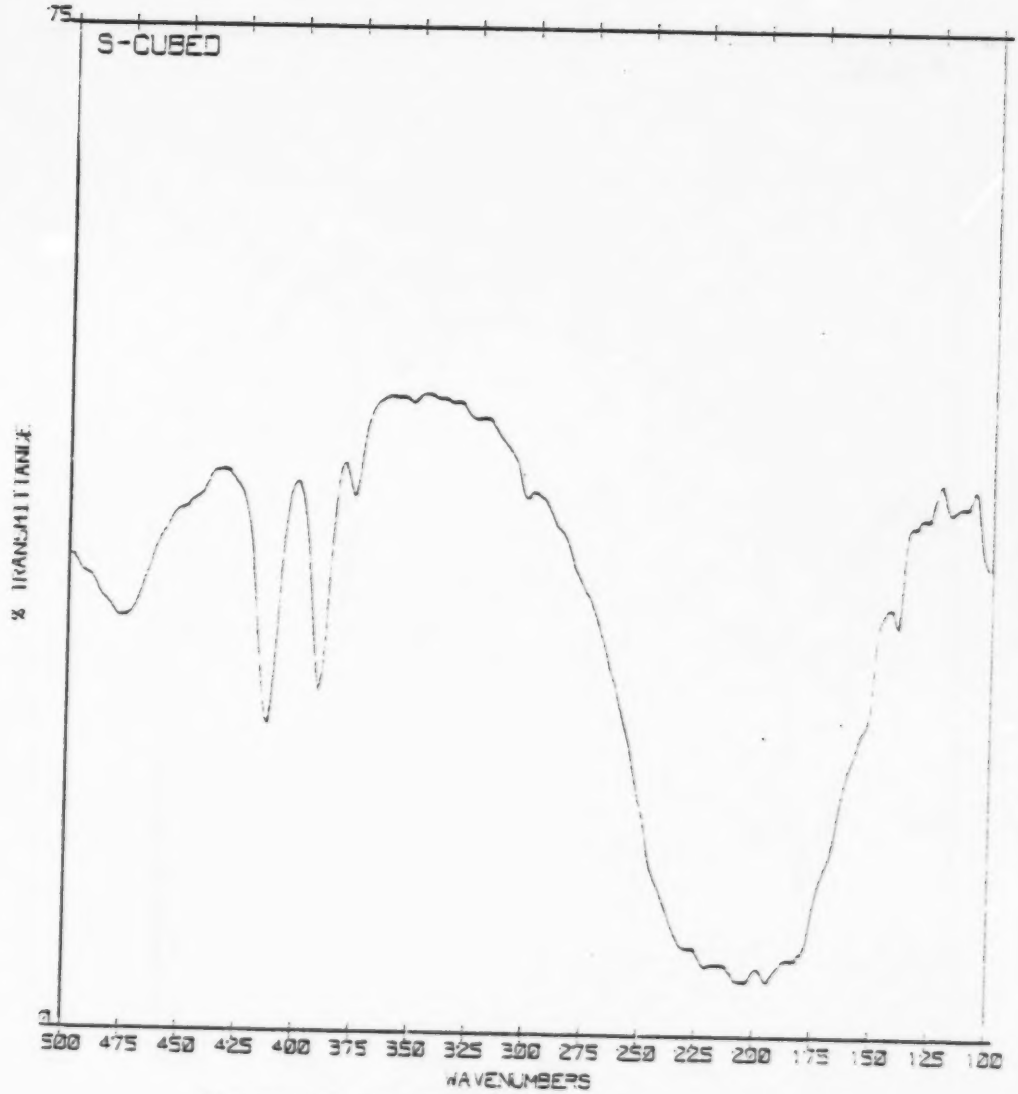

Figure A13-b. SODIUM CHROMATE

SFL=FNCC
NSCANS=100
PL=T

RES=4 CP

SFL=TTAIR
NSCANS=100
4/15/91 11:35:20

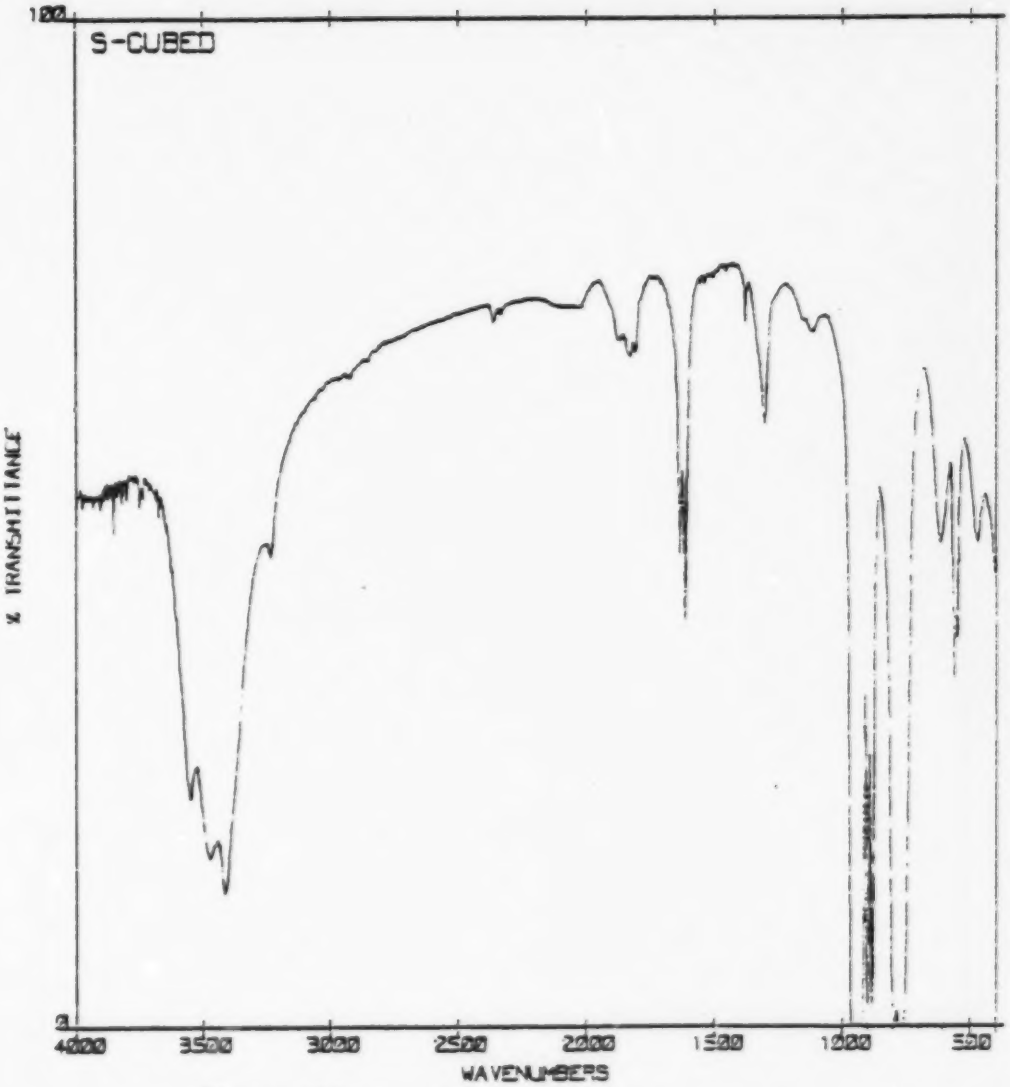

Figure A14-a. SODIUM DICHROMATE

SFL=DICR
NSCANS=100
PL_4=T

RES=4 DP

RFL=PAIR
NSCANS=100
4/7/81 10:51:43

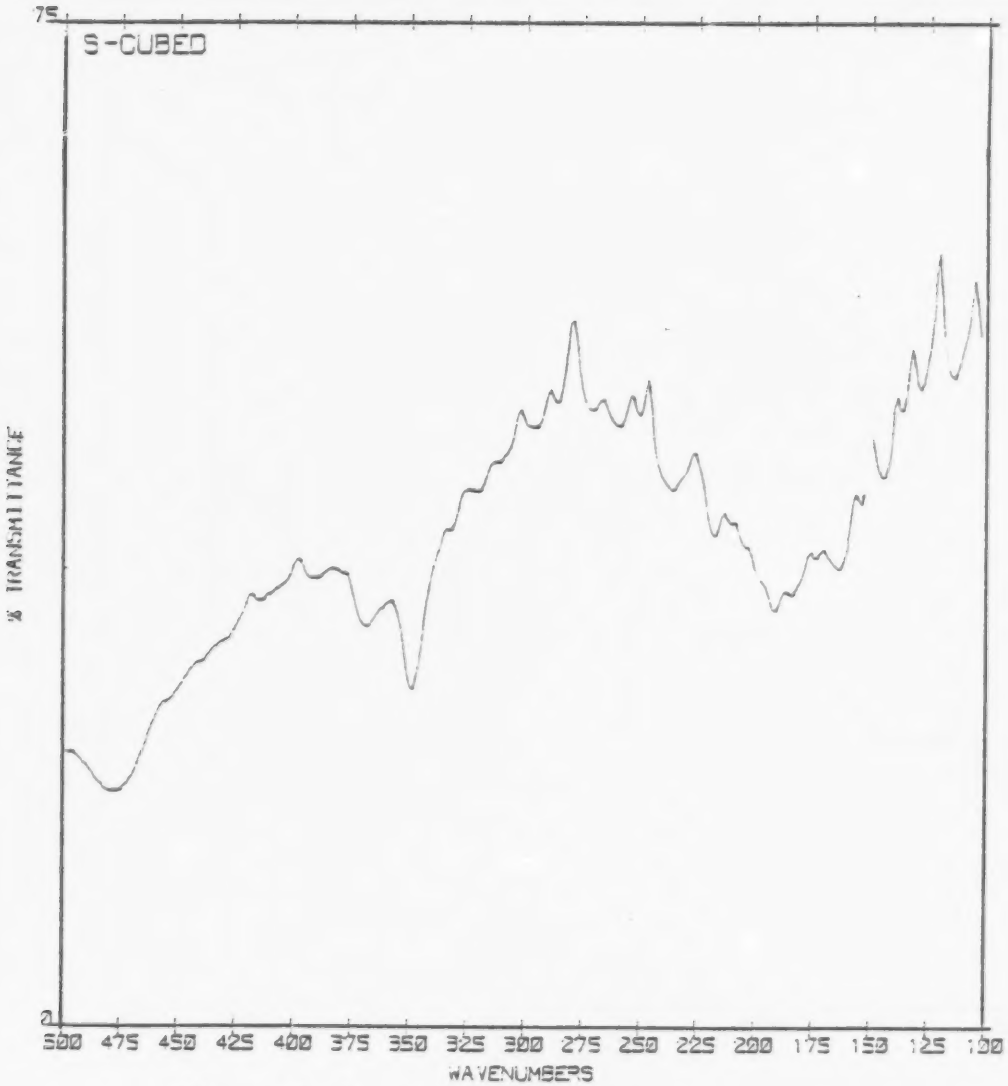

Figure A14-b. SODIUM DICHROMATE

SFL=FNCO
NSCANS=100
PLM=T

RES=4 CP

RFL=TAIR
NSCANS=100
4/15/81 11:43:.5

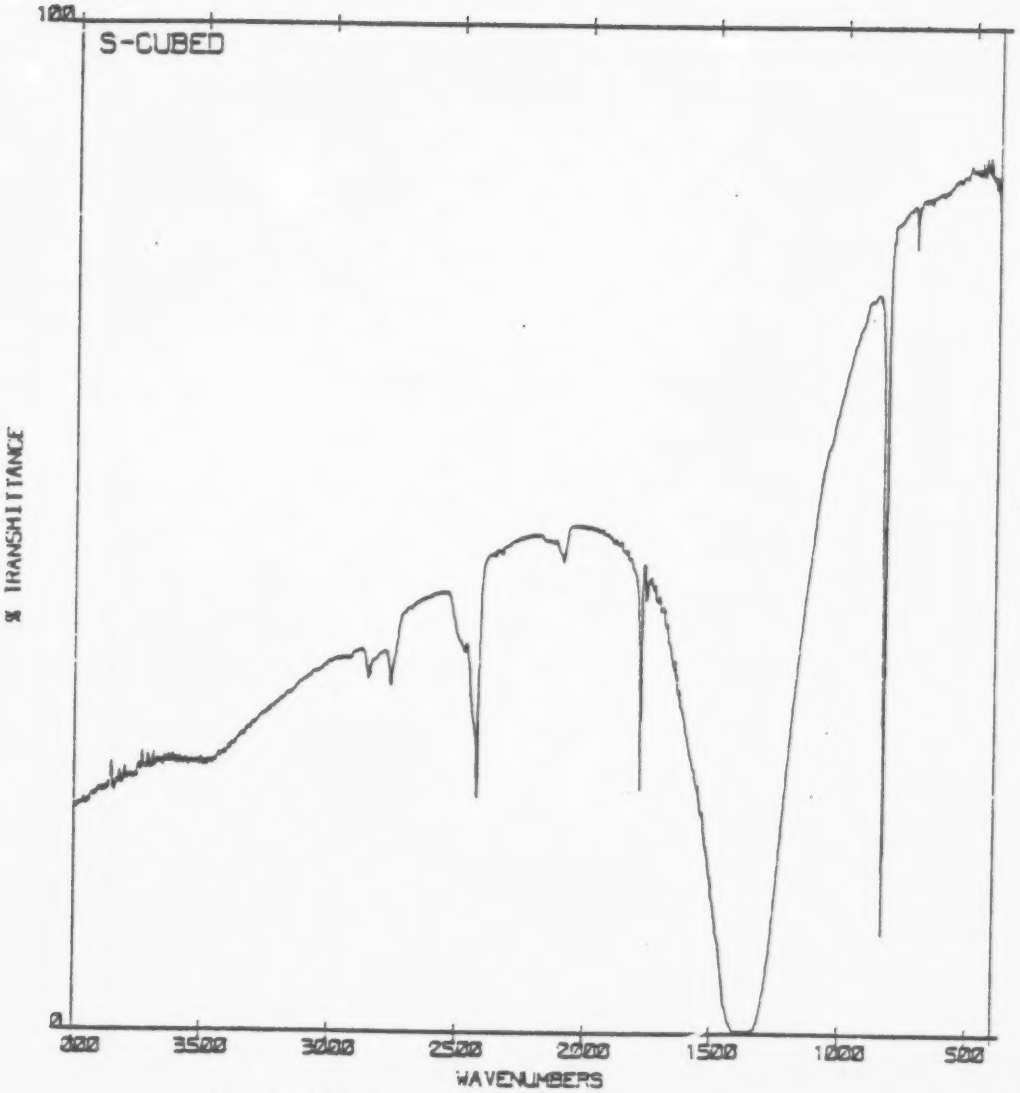

Figure A15-a. SODIUM NITRATE

SFL=XZZ
NSCANS=100
FLM=T

RES=4 DP

RFL=XAIR
NSCANS=100
2/12/81 9:13:49

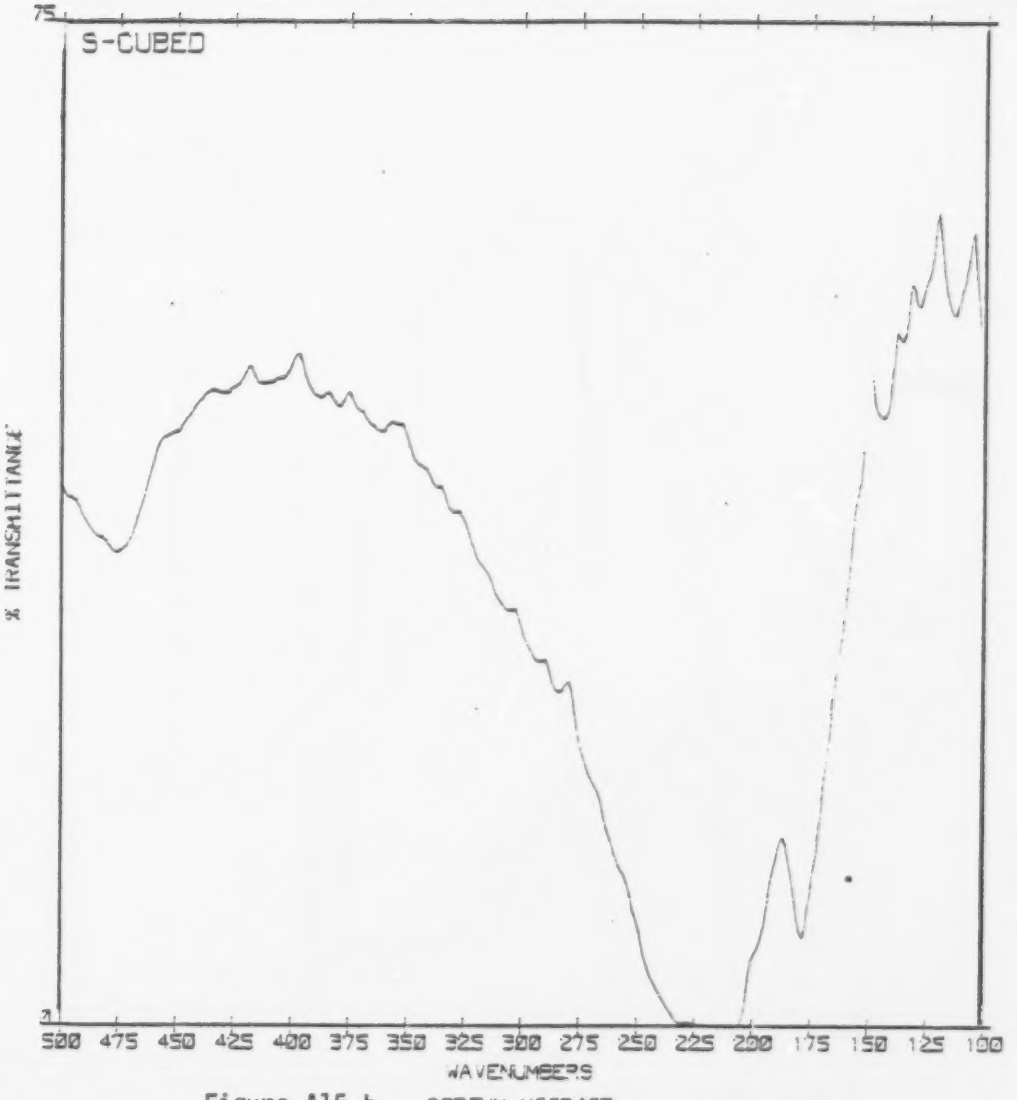

Figure A15-b. SODIUM NITRATE

SFL=FNNO3
NSCANS=100
PLM=T

RES=4 CP

RFL=TAIR
NSCANS=100
4/15/81 11:45:21

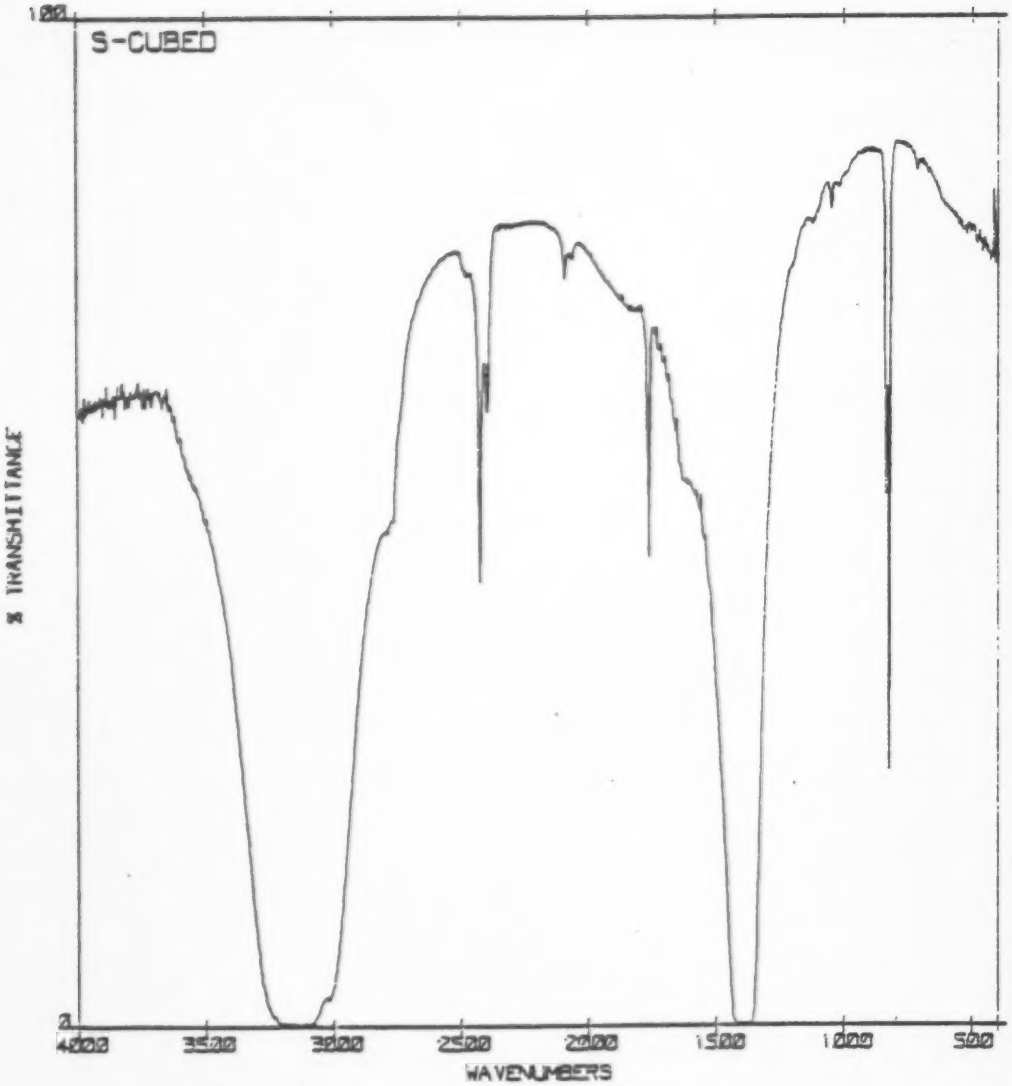

Figure A16-a. AMMONIUM NITRATE

SFL=NH4NIT
NSCANS=100
PL4=T

RES=4 DP

RFL=MAIR
NSCANS=100
3/24/81 15:47:13

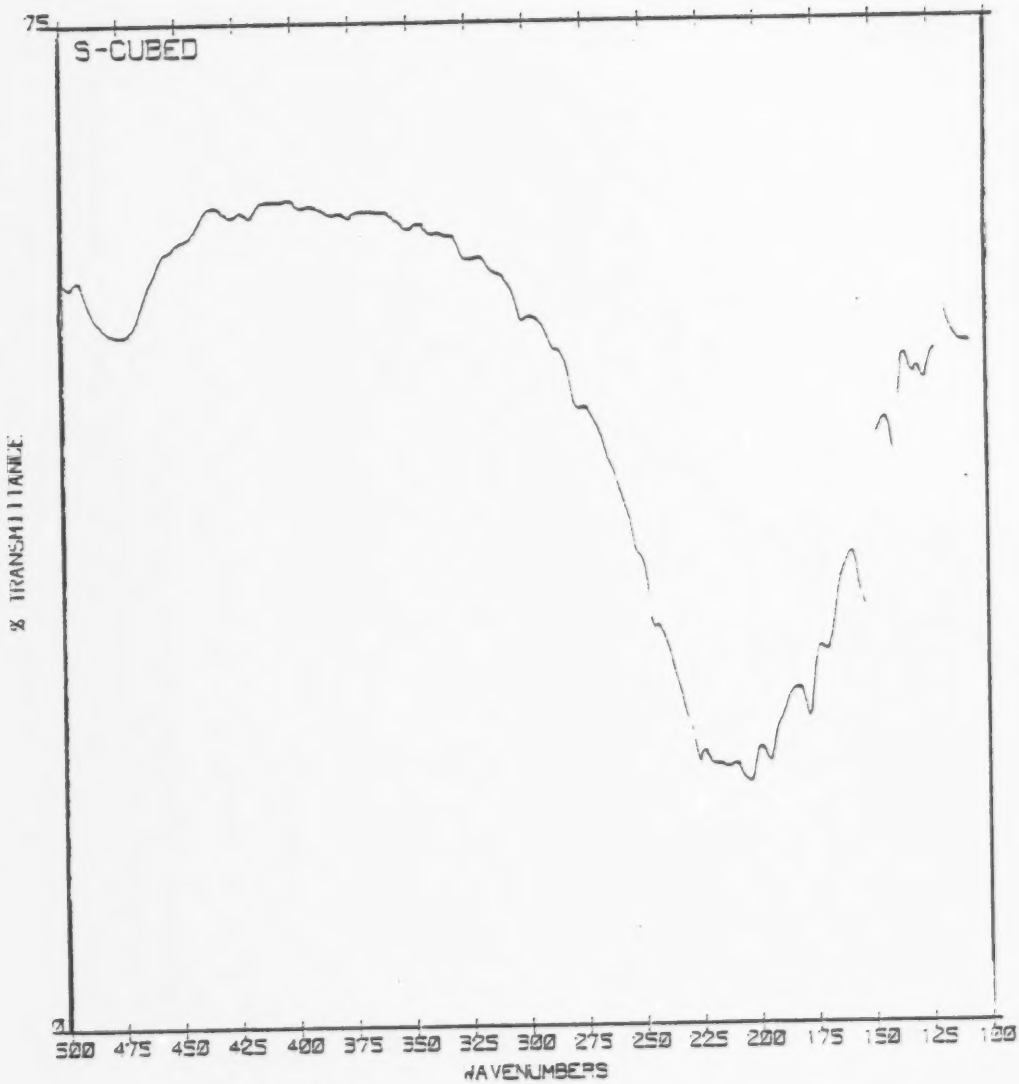

Figure A16-b. AMMONIUM NITRATE

SFL=FNHNO
NSCANS=100
PLM=T

RES=4 CP

RFL=CAIR
NSCANS=100
4/16/91 10:18:16

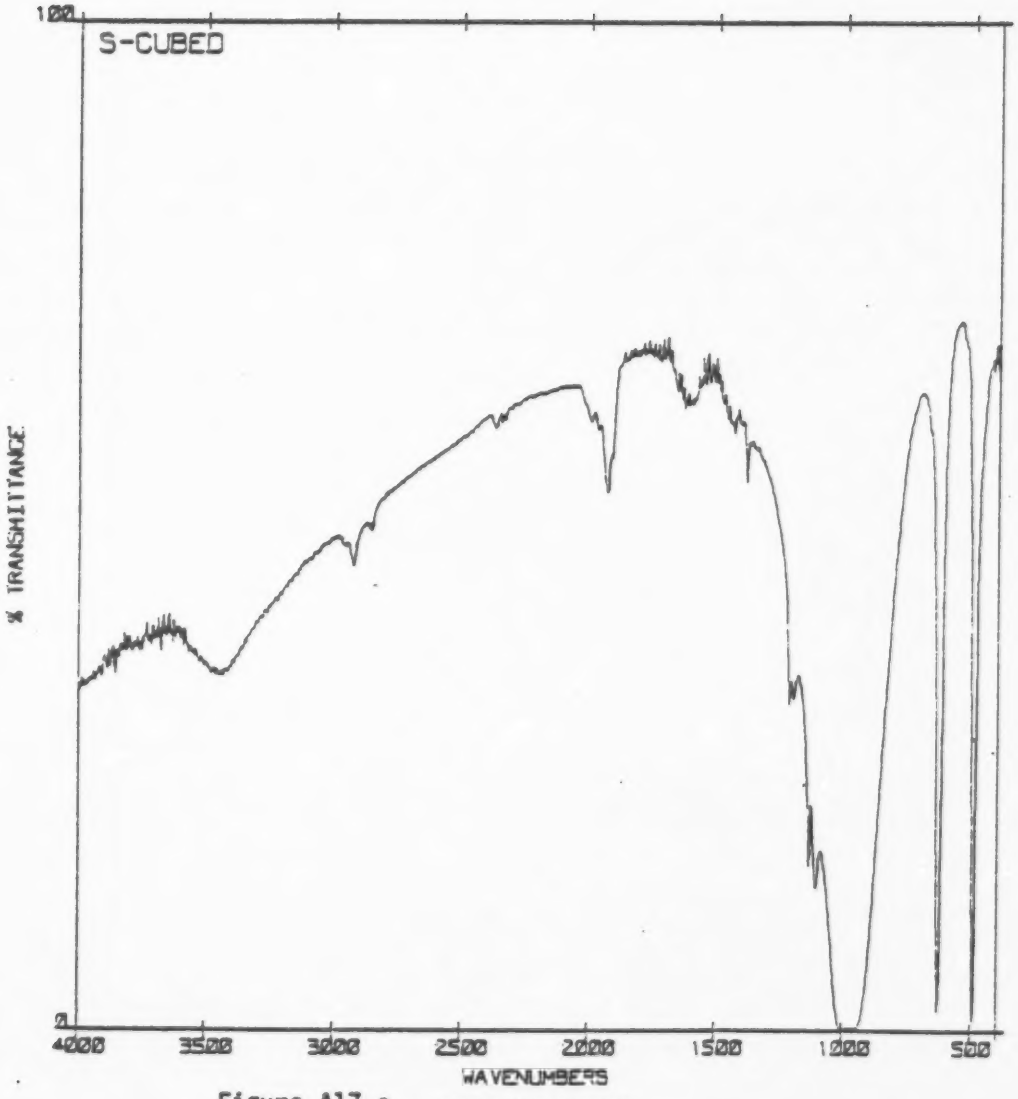

Figure A17-a. SODIUM SULFITE

SFL=ZAA
NSCANS=100
PLM=T

RES=4 DP

RFL=XAIR
NSCANS=100
2/12/81 9:39:9

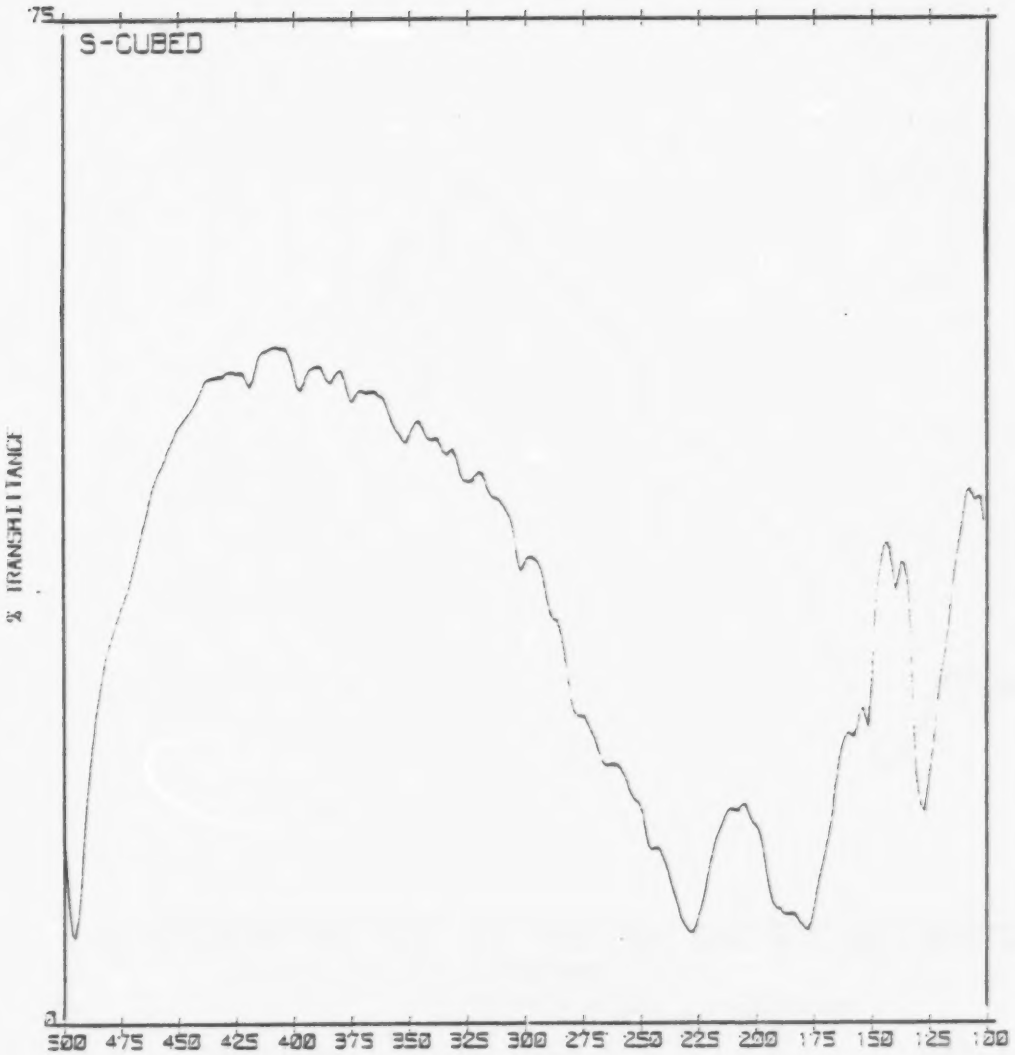

Figure A17-b. SODIUM SULFITE

SFL=NSO3
NSCANS=100
PLY=T

RES=4 DP

RFL=TTAIR
NSCANS=100
4/15/81 11:26:38

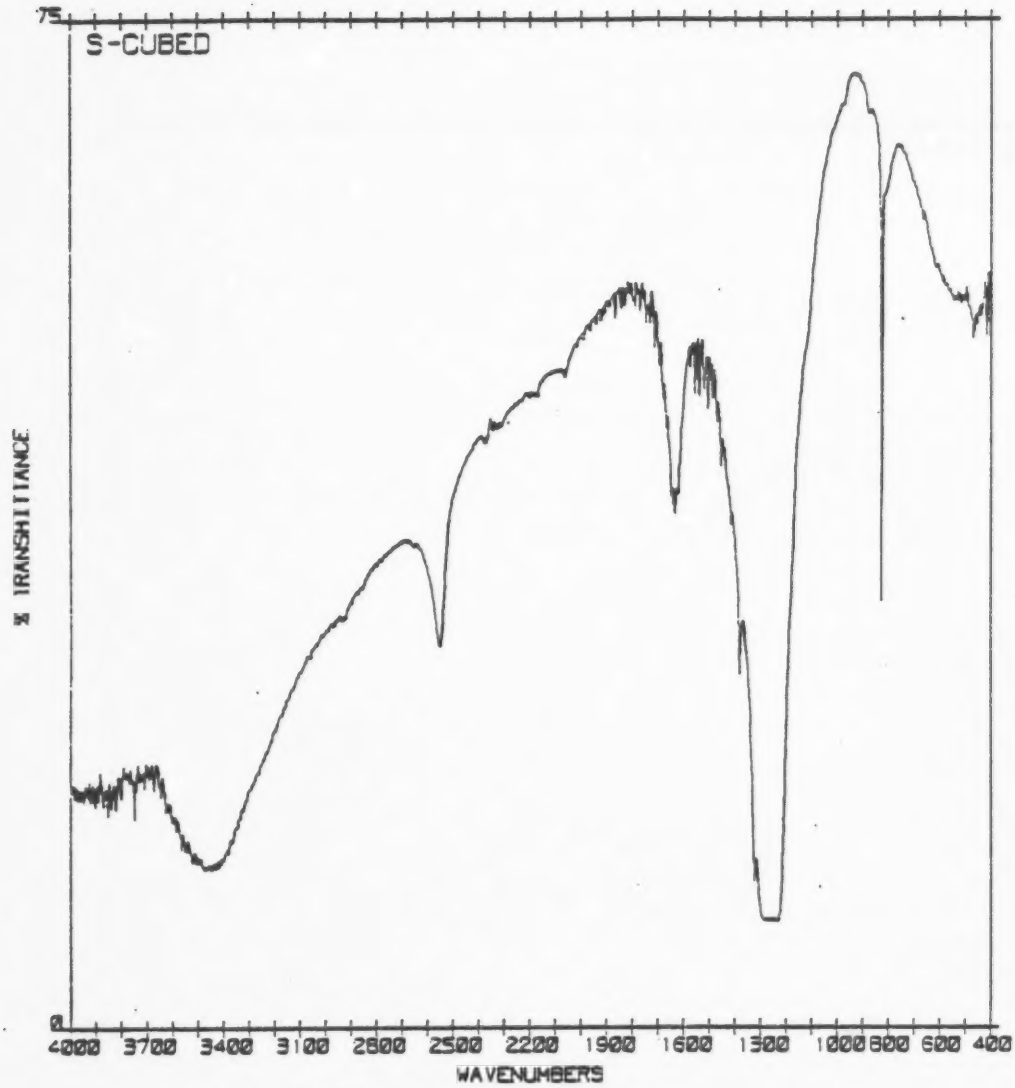

Figure A18-a. SODIUM NITRITE

SFL=OUYQ
NSCANS=100
PH_M=T

RES=4 DP

RFL=IUAIR
NSCANS=100
10/5/81 13:23:25

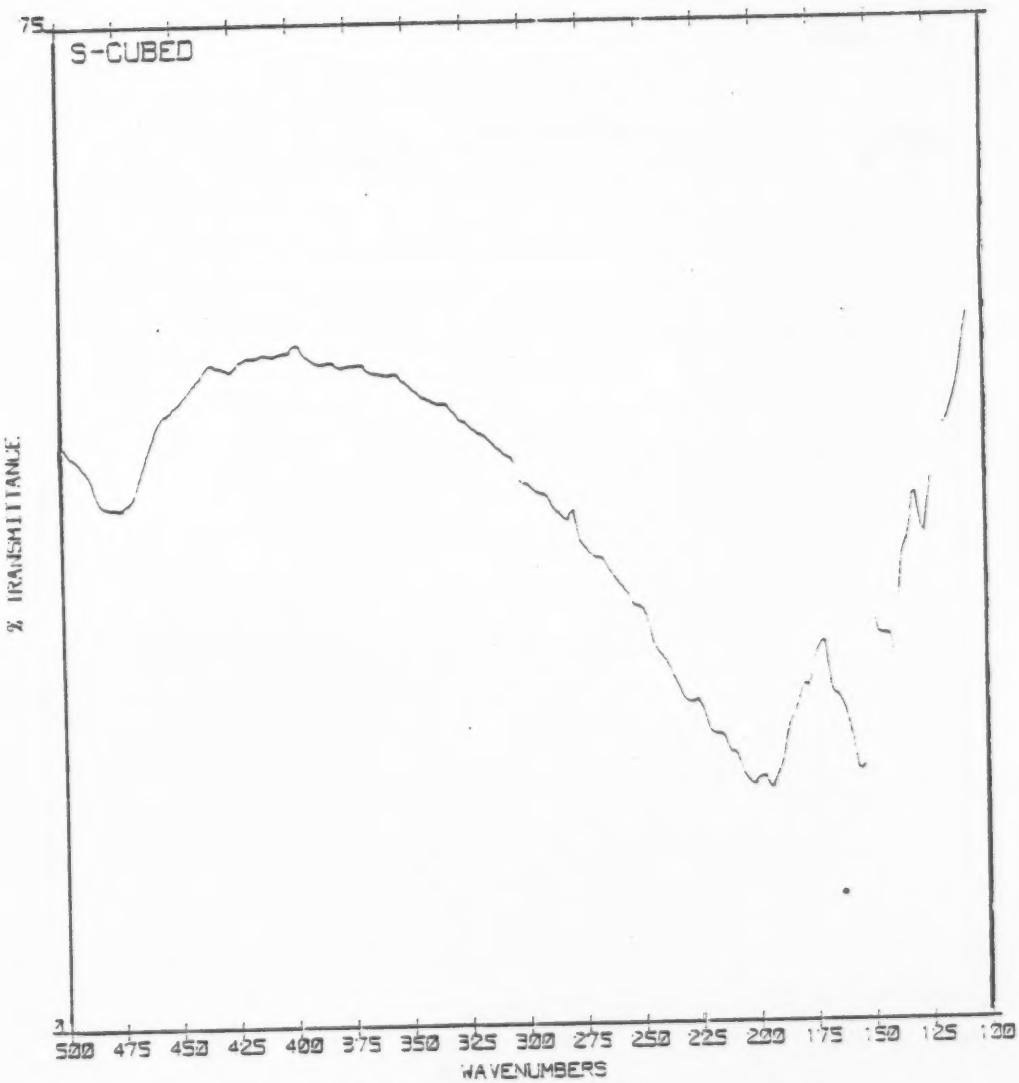

Figure A18-b. SODIUM NITRITE

SFL=FNNO2
NSCANS=100
_PLM=T

RES=4 DP

RFL=CAIR
NSCANS=100
4/16/91 10:7:40

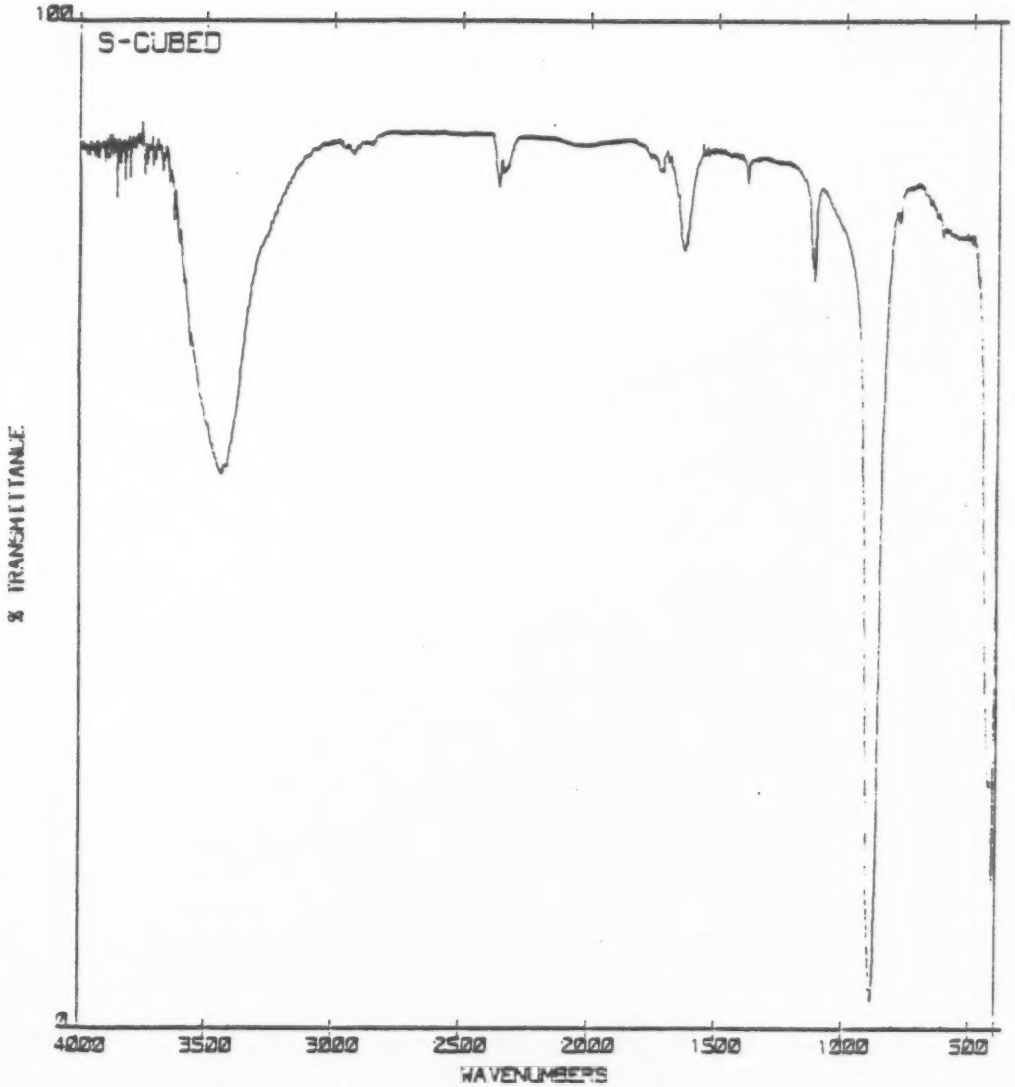

Figure A19-a. SODIUM SELENATE

SFL=NASE
NSCANS=100
PL_M=T

RES=4 DP

RFL=MAIR
NSCANS=100
4/1/91 14:45:0

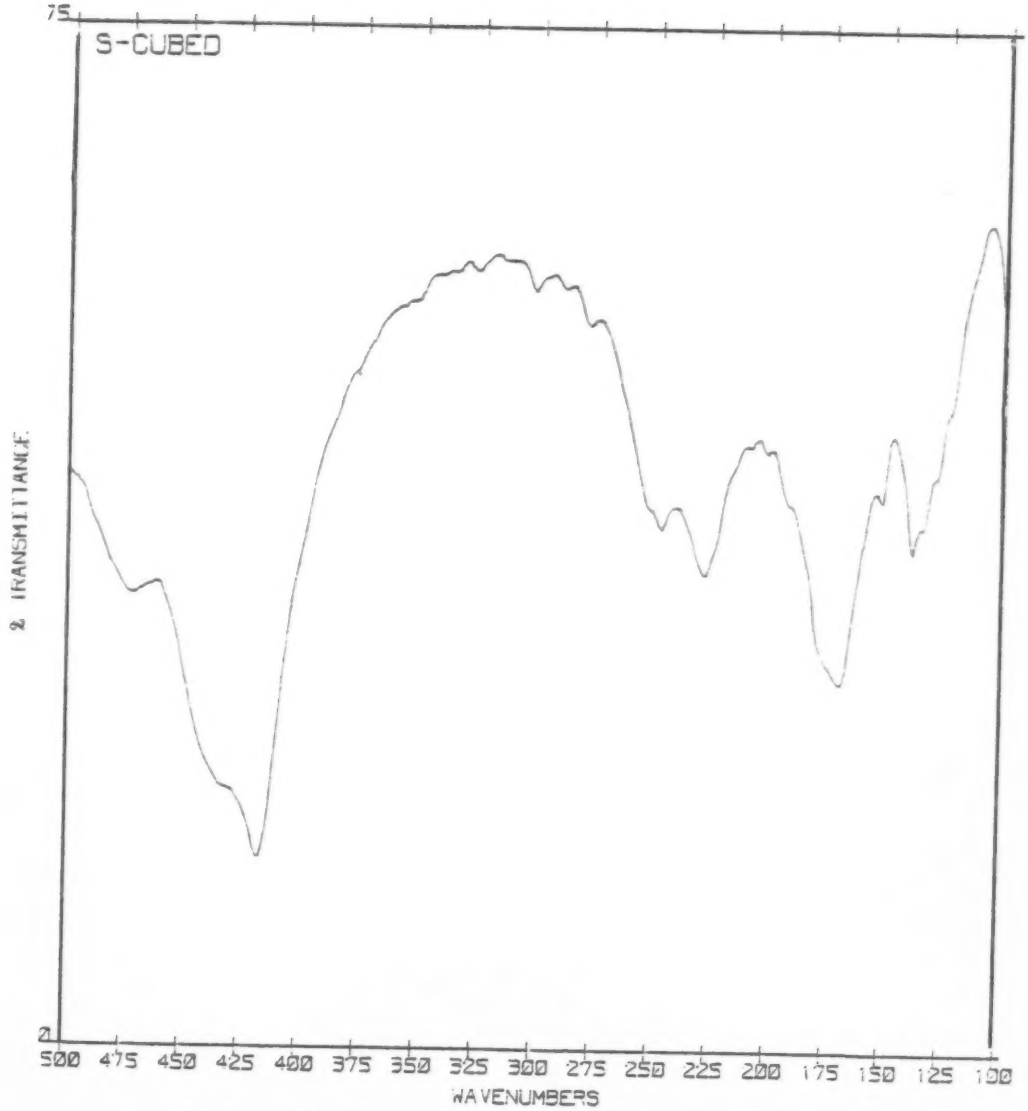

Figure A19-b. SODIUM SELENATE

SFL=FNSEL
NSCANS=100
PLM=T

RES=4 DP

RFL=TTAIR
NSCANS=100
4/15/91 11:33:17